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IMPROVEMENT OF TREATMENT OF FOOD
INDUSTRY WASTE

Sidney B. Tuwiner

RAI Research Corporation

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Laboratory studies were conducted to determine the feasibility of reducing the COD demand of cheese whey waste generated from dairy processing plants. Three primary processing variables were studied; ~~these were~~ agitation, temperature and current density. Results indicate electrolytic oxidation efficiency was best at 70°C, agitation at 9.6 feet per second and a current density of 9.5 amperes per square foot (equivalent to 6 amperes in the test cell investigated). Concentration of 60 percent of the whey protein was also possible by collection of the froth produced during electrolysis. This mechanism of COD reduction could afford recoverable protein from the whey. Carbon adsorption of the electrolyzed whey was also shown to be extremely effective in reducing the COD. The carbohydrates after oxidation to carboxylic acids are very readily adsorbed, the carbon loading being in excess of that expected for secondary effluents. The feasibility of combining the electrolytic oxidation with froth collection and carbon adsorption is proposed as a possible attractive procedure for recovery of values from the whey. (Boydston-EPA)		
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May 1974

IMPROVEMENT OF TREATMENT OF FOOD INDUSTRY WASTE

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ABSTRACT

Laboratory studies were conducted to determine the feasibility of reducing the COD demand of cheese whey waste generated from dairy processing plants. Three primary processing variables were studied; these were agitation, temperature and current density. Results indicate electrolytic oxidation efficiency was best at 70°C, agitation at 9.6 feet per second and a current density of 9.5 amperes per square foot (equivalent to 6 amperes in the test cell investigated).

Concentration of 60 percent of the whey protein was also possible by collection of the froth produced during electrolysis. This mechanism of COD reduction could afford recoverable protein from the whey.

Carbon absorption of the electrolyzed whey was also shown to be extremely effective in reducing the COD. The carbohydrates after oxidation to carboxylic acids are very readily absorbed, the carbon loading being in excess of that expected for secondary effluents.

The feasibility of combining the electrolytic oxidation with froth collection and carbon absorption is proposed as a possible attractive procedure for recovery of values from the whey.

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SECTION I

CONCLUSIONS

1. The electrochemical oxidation of the organic components of sour whey may be technically feasible.
2. Preliminary estimates indicate the capital cost of an electrochemical system for oxidation may compare favorably with that of a biological system of the same capacity. This is based on a cost of \$78 per daily pound of COD removed.
3. The indicated power requirement for electrochemical oxidation is, within the ranges of temperature and agitation which were studied, approximately 8 kwh per pound COD removed.
4. Electrochemical partial oxidation of sour whey permits recovery of at least half of the protein in a froth concentrate, based on the results of two runs. The solution remaining after froth separation may be treated for final disposal by further electrochemical oxidation and/or by activated carbon adsorption.
5. In the electrochemical partial oxidation of sour whey the primary reaction is that of conversion of lactose to lactonic acid. Secondary reactions result in formation of gluconic and galactonic acids. These are refractory to further oxidation of primary and secondary hydroxyl and the breaking of carbon-carbon bonds.
6. Investigation of very limited scope indicates that for an activated carbon the adsorption of products of partial electrochemical oxidation may be represented by a Freundlich equation within a substantial range of carbon loading.
7. The further oxidation of the acidic products of partial oxidation of whey is highly dependent on temperature for the electrode system and conditions of this study. A practical method of electrochemical oxidation to remove COD requires a temperature of at least 35°, and preferably 50° C.

8. The electrode system of this investigation was designed with alternate layers of expanded-metal anode and cathode separated by inert plastic net spacers. This permitted liquid circulation through to the electrode layers. The circulation was provided by propeller and turbine stirrers and the rate of oxidation is dependent on the intensity of circulation as measured by the fps of linear velocity of the agitator.

9. Under the conditions employed in this study, with temperature from 35° - 70°C , agitation intensity from 7.0 - 26.1 fps, and anode current density from 4.75 - 19.0 asf, the electrochemical efficiency of oxidation is not greatly dependent on the pH between about 2.3 - 5.0.

SECTION II

RECOMMENDATIONS

Based on the results and conclusions of this study, and in consideration of the need to alleviate pollution from whey while recovering the valuable components of this material, the following recommendations are made for further study and development:

1. It was shown that 60 percent of the protein of whey can be collected as a 25 percent concentrate in the initial froth generated during electrochemical oxidation of whey. A program should be initiated to investigate this technique of froth collection as a mechanism for recovering whey values and for decreasing the COD of the resulting whey. This would improve the economic feasibility of electrochemical oxidation of the remaining COD.
2. Based on 5 experiments on a bench top scale, electrochemically treated whey produced acids which are adsorbed on Darco G-60 (Atlas Chemical Industries) activated carbon. Further study is needed on this aspect.
3. If the results and conclusions of the present study are confirmed in further bench scale studies, initiate a pilot study of the method of electrochemical total oxidation of whey, using data generated from this study and those proposed above, to establish the economics of the process. This is provided that cost projections and technical feasibility estimated from further bench scale tests compare favorably with alternative methods of whey treatment.

SECTION III

INTRODUCTION

Whey from dairy processing plants constitutes a significant source of water pollution in many areas of the United States. The wastes generated by these plants may be characterized either as concentrated wastes with high solids concentration and BOD, or as dilute wastes which are obtained in rinsing of curds and cleaning of equipment. The problems of handling these two general types of waste are quite different.

Whey remains as the liquid fraction when milk is curdled and the curds are separated by screening. These curds contain most of the casein and fat while the whey contains the lactose, salts, albumin and globulin as well as acid substances, such as lactic acid, which assist the curdling process. Characteristics of the cheese depend on the conditions of curd formation. These conditions do not greatly affect the chemical composition of the whey except with regard to the concentrations of these acids and that of calcium and phosphate.

Sweet whey is obtained when the curdling is primarily with rennet, an enzyme obtained from the stomachs of cattle. Some lactic acid is present, however, to assist in the process. Acid whey is obtained when curdling is produced primarily by lactic acid developed by fermentation of the milk with lactobacillus or by addition of mineral acid. The sour milk is heated and the rate of curdling is a function of both pH and temperature.

It is believed that the applicability of the results of this study is not limited to the specific acid whey which was used inasmuch as acid substances are produced from the lactose regardless of the initial acidity.

Table 1 indicates the percent of various components of a typical whey. Other types of whey may vary from this analysis somewhat. Probably the most variable component is the protein content which depends considerably on the conditions of curdling.

TABLE 1

Composition of Cheddar Cheese Whey

<u>Components</u>	<u>Percent</u>
Total solids	6.57 - 7.13
Protein	0.82 - 0.95
Fat	0.12 - 0.36
Lactose	4.62 - 5.05
Acid as Lactic	0.144 - 0.236
Ash	0.366 - 0.649

This study is intended to develop a method of treatment of the concentrated waste and, specifically, the whey which is produced in cheese-making. In the non-dairy food processing industry, there are similar wastes such as blood from slaughter houses and liquor from the blanching of vegetables, which may be amenable to similar methods of treatment.

It is desirable, whenever economic circumstances permit, to recover the value in these wastes. For example, products for human or animal nutrition are often produced by concentrating and drying. To a considerable extent, the recovery of whey solids as dried whole whey and as specialty food products is being practiced. One such specialty is partly desalted whey solids for infant feeding.

The capital cost of equipment for evaporation and drying is extremely high per unit capacity in small sizes, resulting in high unit operating cost in small plants attempting recovery of whey solids. Under existing circumstances, the value of the whey solids recovered is far less than the cost of evaporation and drying unless the scale of operation is quite large. As a consequence, a large amount of whey is discharged to waste.

Discarded whey is sometimes digested anaerobically in septic tanks. This results in a relatively minor reduction of BOD.¹ Aerobic treatment is possible also but the whey must be diluted by some fiftyfold to permit the organisms to proliferate.² Here again the cost of treatment is exceedingly high, particularly in the smaller size plants, both in capital and operating costs.

This investigation was conducted to develop an electrochemical method of oxidation of the organic components of whey. In the proposed system, the electrolytic process is designed to convert these organics into carbon dioxide, water and nitrogen. The process may be either batch or continuous, and there is no need for use of chemicals or the separation of solids or for solid-waste disposal.

Power, which is the principal item of operating expense in this system, is available in most rural areas. The system may be used under constant load or with off-peak power, depending on the relative economy. The power is used to reduce the BOD and COD.

During the treatment process, the organic components of the whey are converted in stages, and there is a wide variety of substances present at any time. In the conversion of any substance by oxidation, the oxidized product or products constitute a smaller oxygen demand than the parent substance. It is possible to follow the course of the conversion by monitoring the COD. It is possible also to estimate the current efficiency by noting that the faraday equivalence of oxygen is approximately 1,520 ampere-hour per pound of oxygen (3.35 amp-hr/gram). Ideally, this amount of current should reduce the oxygen demand of the whey by exactly one pound.

The power requirement depends on the cell voltage. It is to be expected that this will always exceed the decomposition potential for water, which is 1.229 volts. With these assumptions, the minimum power usage must be 1.867 kwh/lb oxygen demand reduction (4.12 watt-hr/gram). In practice, the power requirement is several times this minimum as is shown in Table 2, which is a summary of results of the present study.

This study examined the effects of various parameters such as temperature, agitation and current density on current and power efficiency. With this information, the power requirement can be optimized. The capital cost for the cell and electrodes decreases as current density increases; however, the power cost increases. The system is optimized

when the incremental power cost resulting from increased current density equals the incremental saving in cost of financing the capital investment.

SECTION IV

MATERIALS AND METHODS

The system is based on the principle of anodic oxidation of various components of the solution, while hydrogen gas is liberated by reduction at the cathode. Power efficiency requires prevention of concentration polarization at the electrodes by stirring and by a design configuration permitting maximum mixing flow. The present anode design, fabricated from expanded titanium sheet platinized for minimum over-voltage, permits good circulation.

To minimize the path of the electrolytic current and thereby minimize the cell voltage, the cathodes which are 14 mesh woven bronze screens, are placed in close proximity to the anode, one cathode on either side. Polyethylene mesh screen is placed between each cathode and the anode to provide uniform spacing while precluding contact of the electrodes and consequent shorting.

Figure 1 represents the configuration of the electrode system and agitator in the glass vessel, which is 12 inches high with an internal diameter of 4.75 inches. Figure 2 represents an enlarged sectional view of this electrode system showing the separation of the cathode screening from the platinized anode.

The electrode system was made from an anode, 6 x 24 inches, of platinized expanded titanium sheet with a facing cathode of 14 mesh woven copper wire screen on each side of the anode. The copper screening was cut to the same size as the anode and each cathode was separated by a layer of polyethylene mesh from the opposing anode face.

This multilayered composite, consisting of two cathodes, two layers of polyethylene mesh and an anode, was coiled into a spiral to fit within the 4.75 inch diameter at one of the vessels. Electrical contact was provided by one inch wide tabs, one to each electrode. The anode tab was of platinized titanium sheet welded to the anode, and the cathode

tabs were an integral part of the woven screening of the cathodes. The three tabs rose upward from the upper edges of the coiled electrode layers and were provided with copper lugs for connection with the current source.

Each assembly included an overhead stirrer mounted to provide an agitator within the spirally coiled electrode system. This was designed to provide circulation of the whey radially outward from the agitator and through the multiple layers of the electrode system.

The details of the electrode system are shown in Figure 2 which is a sectional representation, showing the electrodes and separators in their spatial relationship, and indicating the direction of flow of in process whey through the electrode layers and over the active electrode area. This configuration is one which permits the gases which are generated (hydrogen, nitrogen and carbon dioxide) to rise within the electrode system and supernatant whey.

This configuration of the electrode system, involving a layered assembly of foraminous electrodes and spacers, and combining the features of freedom of circulation, and of gas release, with close electrode spacing, is novel.

The working volume in all experimental runs was 3 liters. A constant liquid level was maintained by automatic additions of makeup water equal to the evaporation. The temperature was controlled thermostatically and the cell current was controlled by a power supply.

Inasmuch as the lactose is the principal component resisting oxidation and constitutes the major fraction of the whey solids, minor variations in whey composition do not greatly affect the treatment requirements. The process requirements are thus approximately the same for most types of whey.

The method of preparing whey used during this investigation consists of the addition of concentrated HCl to raw milk and subsequently holding the milk at $49^{\circ} \pm 0.25^{\circ} \text{C}$ for 16 hours. At the end of this time the curdled milk is filtered and the curd is discarded. The COD of the whey produced in this way is approximately 62,000 mg/l.

FIGURE 1
ELECTROLYTIC OXIDATION CELL

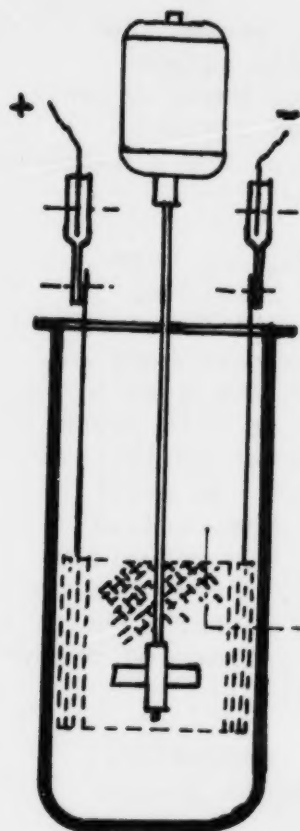
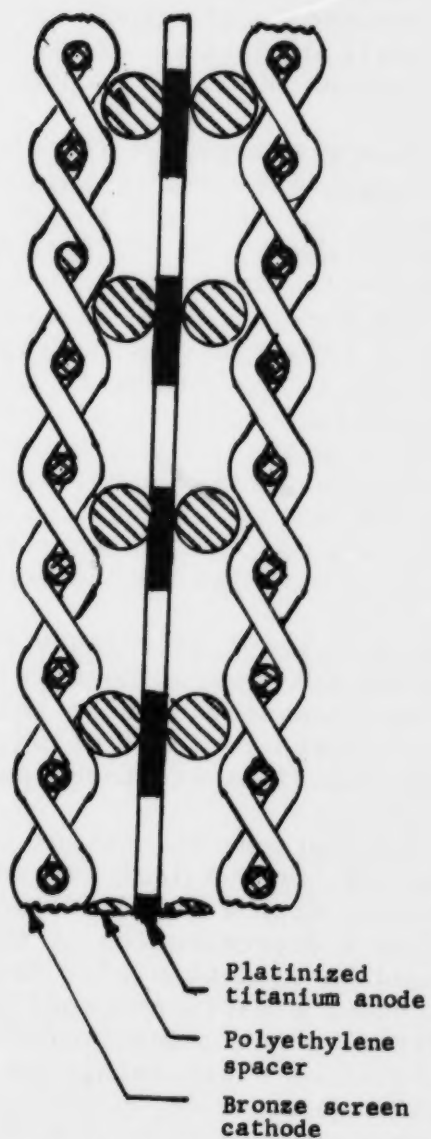


FIGURE 2 - SECTION AA
ELECTRODE AND SPACER DETAIL
ENLARGED



Process Parameters

In all 25 experimental runs conducted in this study, the volume of whey was 3 liters, the anode area 244 square inches and the cathode area 241 square inches; these areas were computed on the basis of the total wetted surface. The overall dimensions of the anode and each of the 2 cathodes were 6 inches by 24.25 inches.

The parameters explored for electrolytic oxidation were temperature, time and agitation. During the period of treatment, the decrease in COD was measured as a function of time to determine efficiency. Each 3.35 ampere-hour of current is theoretically capable of oxidizing one gram of COD. One ampere-day is similarly equivalent to 7.16 grams of COD. Therefore, for a 3 liter batch, theoretically, each ampere-day is equivalent to 2,900 mg/l of COD. In practice, the reduction of COD is always less than the theoretical. The ratio of the actual, to the theoretical, COD reduction is the current efficiency. Some inefficiency arises due to use of the anode current in producing oxygen rather than in eliminating COD and by the reduction at the cathode of products previously oxidized at the anode.

The anode current efficiency is affected by temperature, agitation and current density. These parameters govern both the anode and cathode reaction kinetics. The current efficiency and the rate at which the COD falls are, therefore, complex functions of these operating vehicles.

These evaluations of current efficiency and energy are based on the COD, or chemical oxygen demand. This is obtained in accordance with a standardized analytical method which is based on a determination of the quantity of chromic acid consumed in oxidation of a sample in a solution at the boiling point under prescribed conditions. This quantity is then converted to equivalents of oxygen. Current efficiency is calculated as a percentage of a gram-equivalent of COD reduction per faraday. Energy efficiency is expressed as kwh per pound COD reduction.

A few isolated tests were performed to determine the feasibility of protein recovery from acid whey by collecting the

froth generated by the gas evolved from the electrolytic cell. This froth was recovered by skimming with a spatula until the froth appeared to be barren. The protein-depleted whey, partially oxidized electrochemically, was then tested for its treatability using Darco G-60 activated carbon as an adsorbent. An adsorption isotherm at 25°C was obtained by determination of the COD of a diluted solution in tests with varying amounts of the adsorbent. This adsorbent, a product of Atlas Chemical Industries, was selected in this program because it is a fairly typical example of an industrial product which has been used in wastewater treatment and in development programs.³¹

As indicated on page 58, the adsorption, A, in mg/gm carbon of COD, is represented as a function of the COD concentration, C, in mg/l, by a Freundlich equation:

$$A = 0.132 C^{1.13} \pm 20\%$$

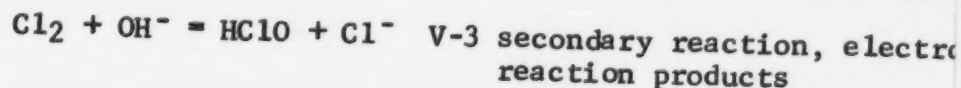
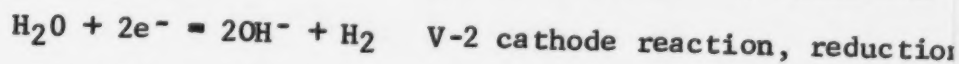
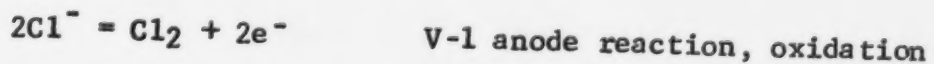
within the concentration limits from 31 - 670 mg/l. The Freundlich equation is used, not because it represents the experimental data better than any other equation but because it is the equation which has been widely adopted in reporting the results of carbon adsorption of wastewater components.³¹

SECTION V

ELECTROCHEMICAL REACTIONS

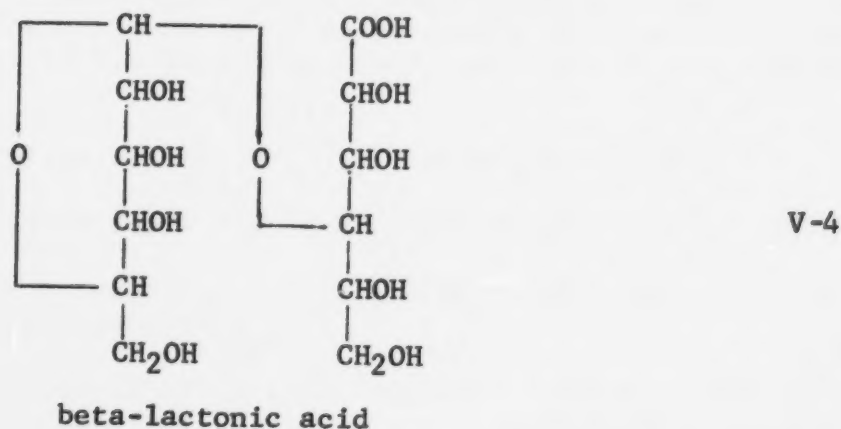
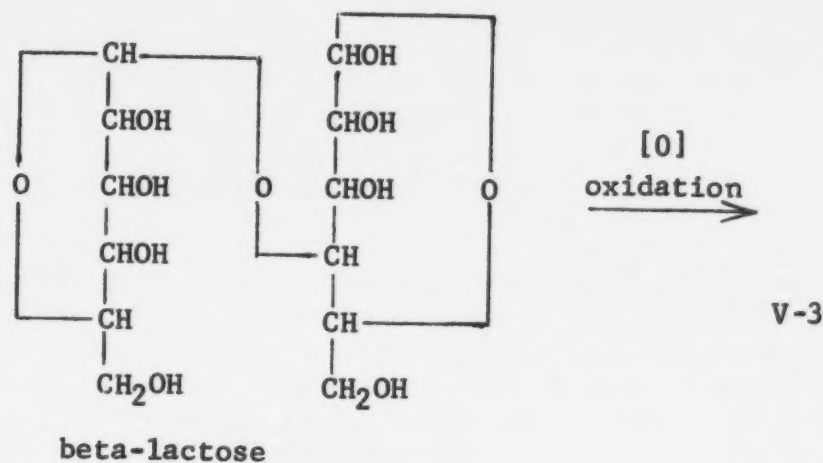
The electrochemical reactions leading to the elimination of COD from whey are numerous because of the complexity of a system which contains products of oxidation and degradation of carbohydrates as well as those of protein components. We have additionally the oxidation of chlorine to hypochlorite, which reacts in turn with organic components whereupon it completes a cycle, returning to chloride.

Hypochlorite is produced when chlorine, generated at the anode, combines with alkali which is produced, together with hydrogen, at the cathode. These reactions may be represented by



The hypochlorous acid, or hypochlorite, is capable of oxidizing various organic components of the system. These components are also capable of being directly oxidized at the anode. There is no simple method of distinguishing experimentally between the two. Some of the chlorine or hypochlorite reacts producing chloramides and chloramines with nitrogenous components. These compounds are capable of serving as oxidants, in turn, for other organic substances.

The principal organic component of whey is lactose, which is very reactive to oxidation, being converted readily to lactic acid as follows:



The reactant, beta-lactose, is here represented as a disaccharide of galactose and glucose, shown as pyranose rings connected by an ether linkage. Oxidation opens the right hand, or glucose, pyranose with hydrolysis of ether linkage, producing galactonic and gluconic acids. Treatment of lactose with bromine and of glucose with chlorine is described and is said to result in production of these acids.^{3,4} Various other sugars have been oxidized similarly,⁵ with acid yields of 50-70 per cent. The formation of the free acids tends to promote degradation. Investigators who have sought to obtain high yields of aldonic acids were led

therefore to buffer the system with barium carbonate or barium benzoate to obtain, for example, yields of 96 per cent for gluconic acid, or 90 per cent for xylonic acids.^{6,7,8,9}

More severe treatment produces oxidation of primary and secondary alcohol groups to aldehydes and ketones. Rhamnose, for example, yields 5-ketorhamnic lactone.¹⁰ With yet more severe treatment the ketones are oxidized to carboxyls with accompanying degradation. Ultimately the organic matter is converted to carbon dioxide and water.

Electrochemical oxidation is the subject of patents,¹¹ claiming the oxidation of sugars in the presence of soluble bromides. Bromine, produced electrochemically, oxidizes the aldose to the aldonic acid and is reduced to bromide. In some cases the yields are almost theoretical.¹² If the reaction is not controlled, di-basic saccharic acids, 2-keto, 5-keto and 5-keto aldonic acids may also be produced.^{13,14}

With platinum electrodes it is possible to obtain a yield of 55 per cent gluconic acid from glucose.¹⁵ The yield, using alternating current with electrodes, is low. The electrolytic oxidation of lactose in bromide solutions is a function of current density, anode material and bromide concentration. According to investigators, oxidation of aldehydes is easily effected in the presence of bromide and iodide ions, but not chloride or fluoride ions.

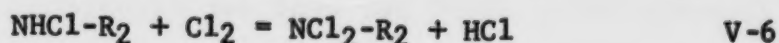
The system for oxidation of proteins is at least as complex as that for lactose and carbohydrates. Proteins are polyamide polymers composed of amino-acid monomers. Hypochlorite or chlorine, produced electrochemically as described above, react at the amide linkages between amino-acid units. They produce N-chloramides, as follows:



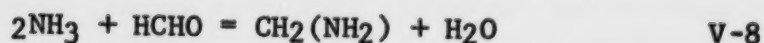
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The chlorination reduces the stability of the amide linkages so that the protein dissociates into smaller fractions, and ultimately into N-chloramino acids. Further reaction with

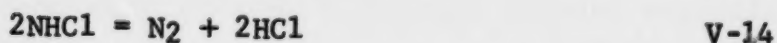
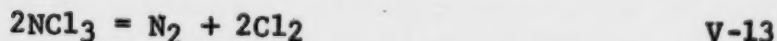
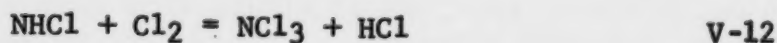
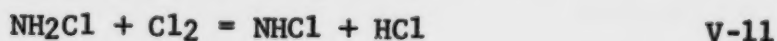
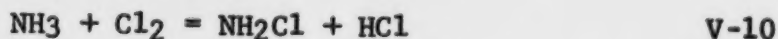
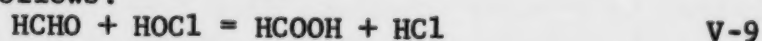
chlorine or hypochlorite produces N,N' - dichloramino acids.²⁸



These compounds, especially the simpler ones, are unstable, especially when the solutions are heated. Among the products are nitrogen, carbon dioxide and acids of lower molecular weight.²⁹ One possible explanation of this result may be indicated by a comparable reaction which occurs when amino-acids are oxidized anodically. In this case, amines are found in the product solution. It is hypothesized that the primary reaction is one of oxidation to ammonia and an aldehyde. For example, aminoacetic acid produces ammonia, formaldehyde and carbon dioxide, as follows:



When chlorine or hypochlorite are present, both the aldehyde and ammonia react, the one to form acid and the other to form chloramine and ultimately nitrogen ³⁰ in a stepwise reaction as follows:



Products of anodic oxidation may be reduced at the cathode in a system in which the anode and cathode compartments are not separated. This reduction may result in a loss of current efficiency since the products of cathodic reduction reverse the desired anodic oxidations.

Thus, carbon dioxide is reduced to formic acid.^{16,17} Keto

groups are reduced to methylene¹⁸ and oxalic acid is reduced to glyoxalic, glycolic and tartaric acid.^{19,20}

The composition of the cathode surface may also influence the reduction kinetics. Ketones are reduced to pinacols when the cathode is lead or mercury, whereas with copper only hydrogen is produced. Antimony and silver manifest an intermediate behavior.^{21,22} In the present program, we have chosen to employ a copper alloy as cathode to avoid side-products such as pinacols or ketonic substances. The difference in cathodic behavior is owing, at least in part, to the higher hydrogen overvoltage over lead and mercury.^{21,22}

SECTION VI

RESULTS

Figures 3-27 are plots of the COD, cell voltage and pH as functions of electrolysis time. It is evident from these that initially there is a decrease in pH during oxidation of the whey. This probably reflects formation of carboxylic acids by oxidation of lactose. These acids are subsequently converted to carbon dioxide and water. Between the initial formation of acids and the final state of oxidation, there is formation of polycarboxylic compounds together with a degradation to compounds with fewer carbon atoms. Simultaneously, there may be reduction of some of these substances at the cathode with subsequent re-oxidation by the anode.

Although the graphs of pH vs. time reflect the influence of the parameters of temperature, current density and agitation, they all indicate in successive stages, an initial pH reduction reaching a minimum or lower limit, a second stage of more or less constant pH, and a third stage in which the pH rises. In the interpretation of these stages it is reasonable to assume that during the first stage acids are produced and that during the third stage acids are destroyed or removed. The chemical, or electrochemical, reactions which are responsible for these changes are outlined in Section V. From these equations it is evident that the formation of acid substances is dependent on the presence of lactose and its derivatives. As these become depleted the acids become subject to a more severe oxidation, producing, ultimately carbon dioxide and water.

The intermediate stage in which there is a more or less constant level of pH may be ascribed to a situation in which the two types of reaction occur simultaneously and in which there may be a significant cathodic reduction of acids as well as degradation from oxidation at the anode or from hypochlorite. The result is the exhibition of a "steady state" in which there are compensating pH effects.

In the graphs which illustrate the reduction of COD with time it is also possible to discern three stages. In the initial stage the rate of reduction is relatively high. Following this there is a more prolonged stage in which the rate of COD reduction is more or less constant and somewhat

less than in the initial stage. In a final stage there is a progressive falling off of the rate of COD reduction.

The rate of COD reduction reflects the rate of electrochemical oxidation, less the rate of cathodic reduction. As indicated in Section V, the initial oxidation of lactose proceeds very readily and, we may assume, with high current efficiency. This accounts for the first stage. Subsequent reduction in stage two occurs with somewhat greater difficulty. Nevertheless the rate-limiting reaction is not necessarily diffusion controlled owing to the fact that there is, presumably, an ample concentration of oxidizable matter in the solution. The third stage is one in which the rate of COD reduction is influenced by the depletion of oxidizable matter in the solution. One would normally suppose under the circumstances, that this rate would be controlled by mass transfer limitations and therefore that the rate of COD reduction would increase with agitation intensity and that this increase would occur especially at high current density.

When reference is made to the graphs of Figures 3-27 it is apparent that there is no simple relationship of current density or of agitation intensity to the current efficiency. Of course, the rate of COD reduction invariably is increased by an increase of current density. However, the current efficiency, which measures the efficiency of current utilization, first increases at low current density and decreases at higher density beyond the point of maximum efficiency. As a further indication of the complexity of the system all of these are affected by agitation intensity and, more especially, by temperature.

The configuration of the electrodes and the materials of their construction are also undoubtedly very important parameters. However, the scope of this investigation did not permit the study of their effects. One electrode system, as described in Section V, was used in all of the runs.

FIGURE 3 RUN: 9
Electrolysis of Acid Whey - Voltage, COD and pH vs Time

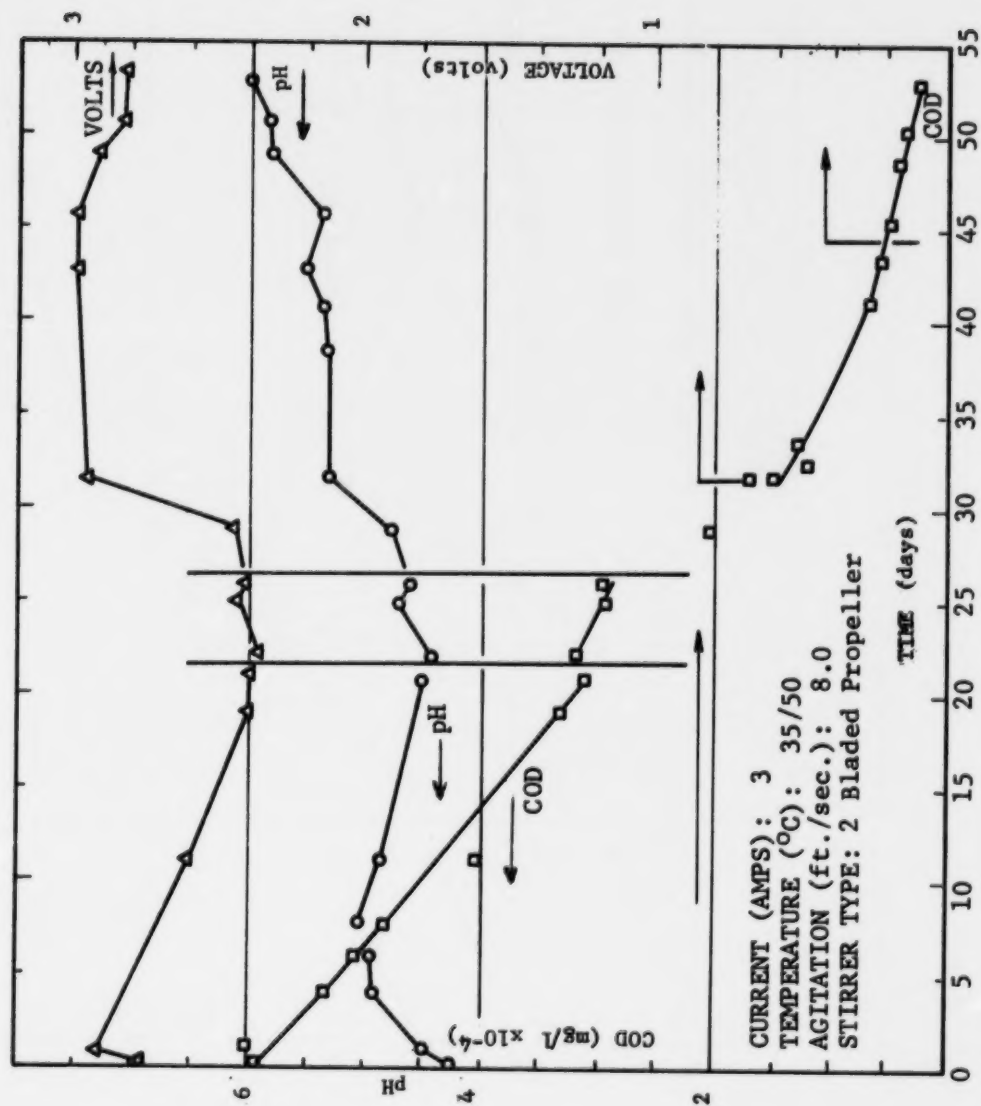


FIGURE 4 RUN: 11
Electrolysis of Acid Whey - Voltage, COD and pH vs Time

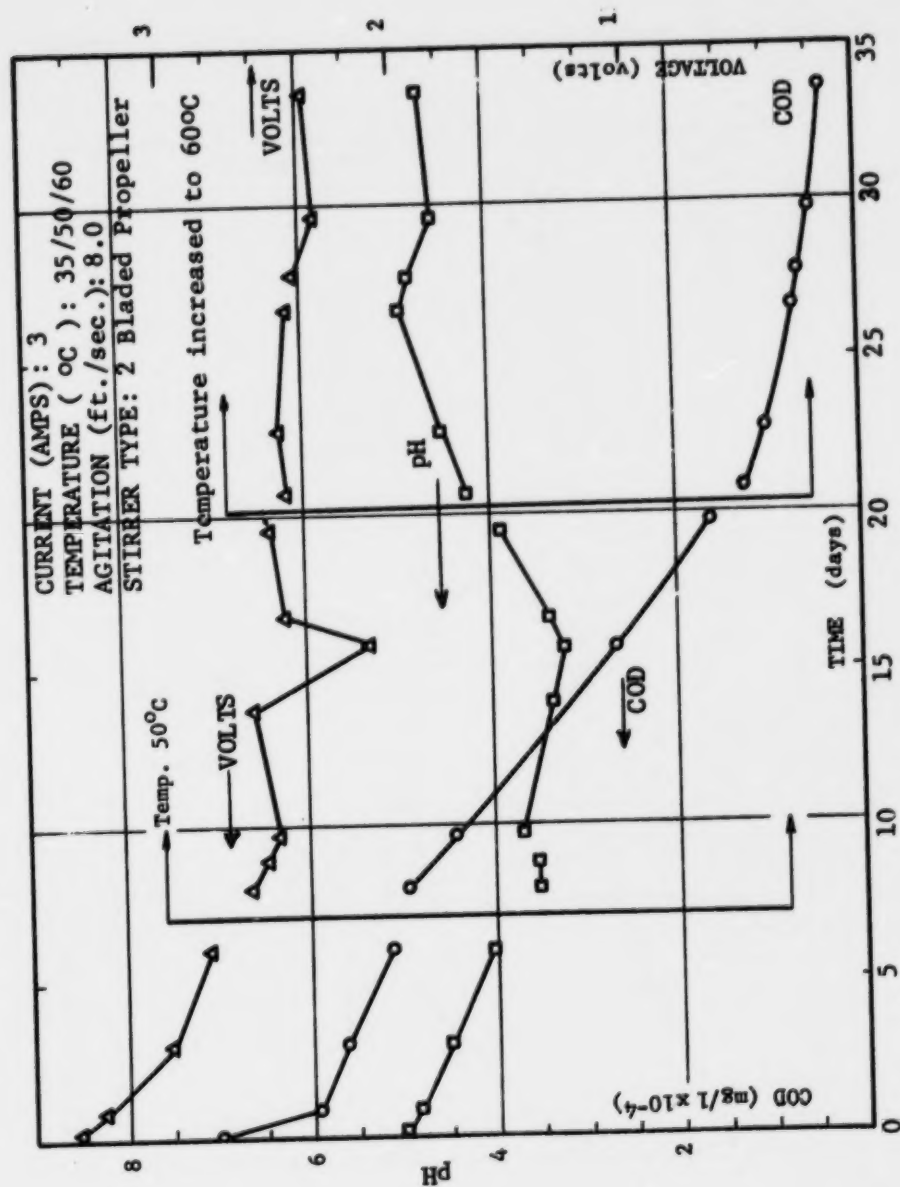


FIGURE 5 RUN: 12
Electrolysis of Acid Whey - Voltage, COD and pH vs Time

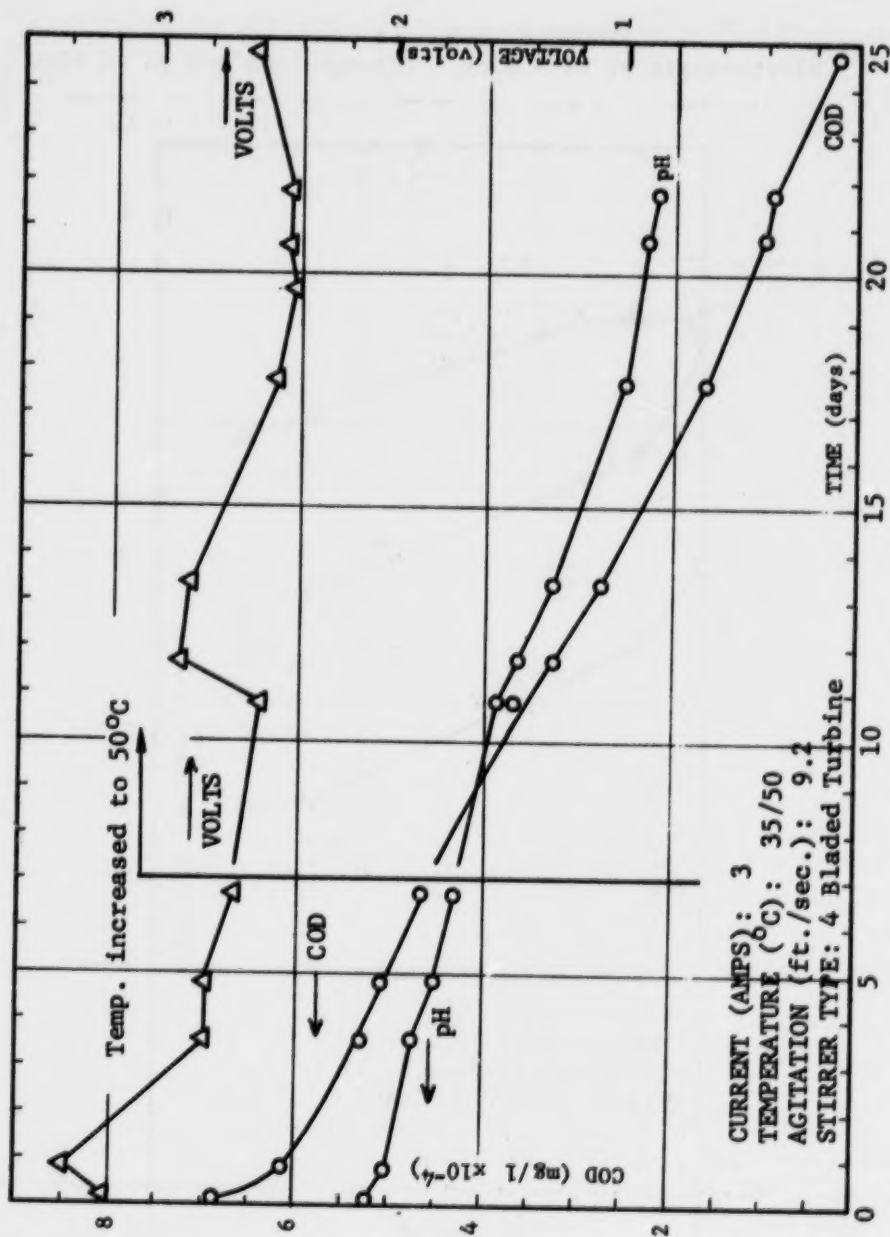


FIGURE 6 RUN: 13
Electrolysis of Acid Whey - Voltage, COD and pH vs Time

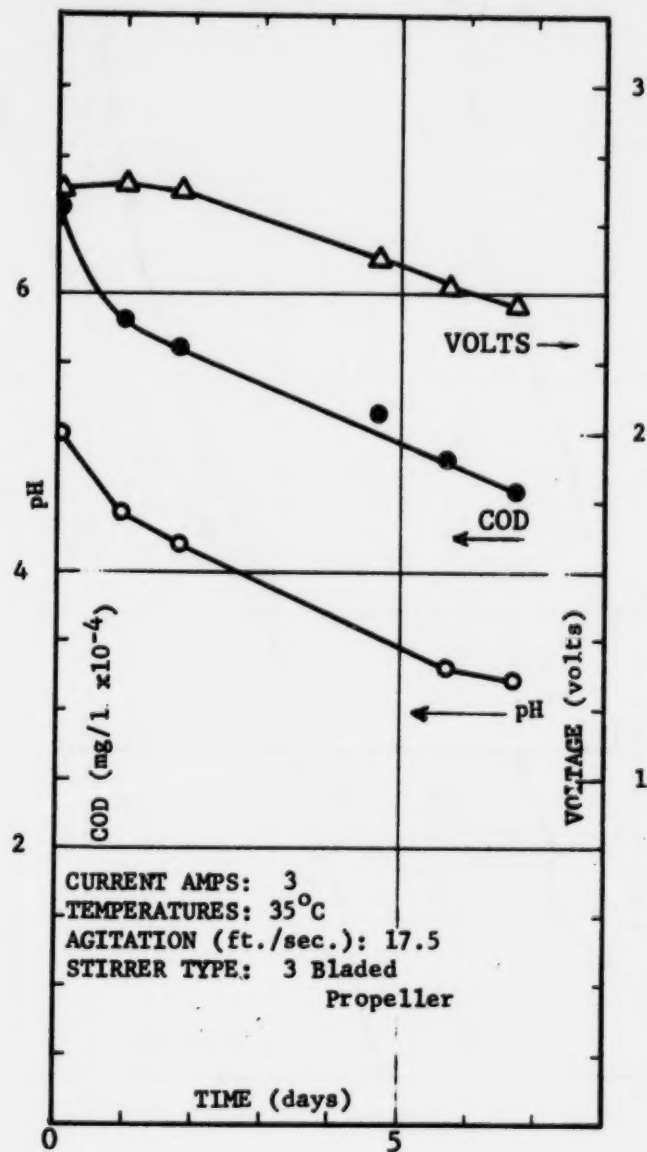


FIGURE 7 RUN: 14
Electrolysis of Acid Whey - Voltage, COD and pH vs Time

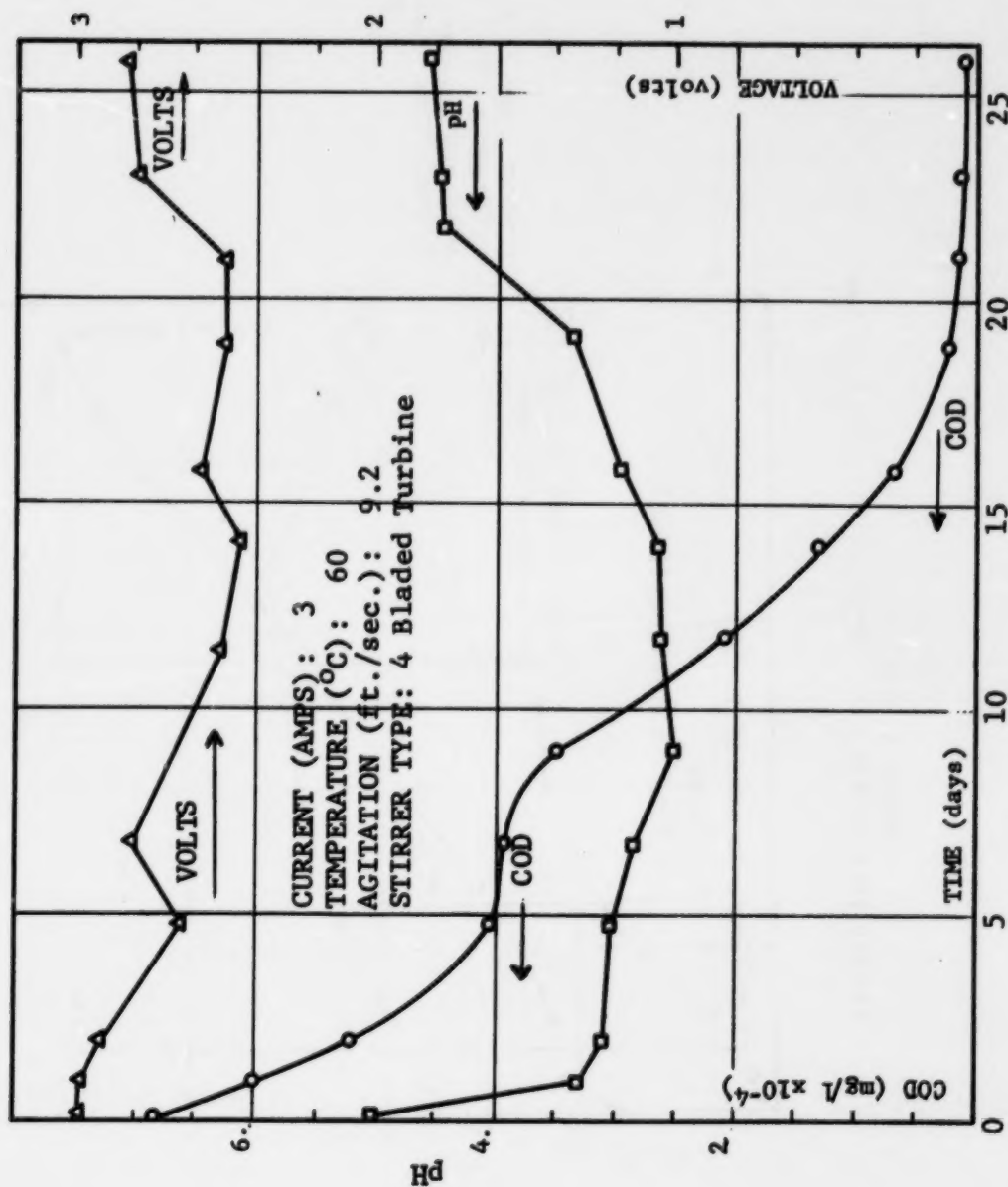
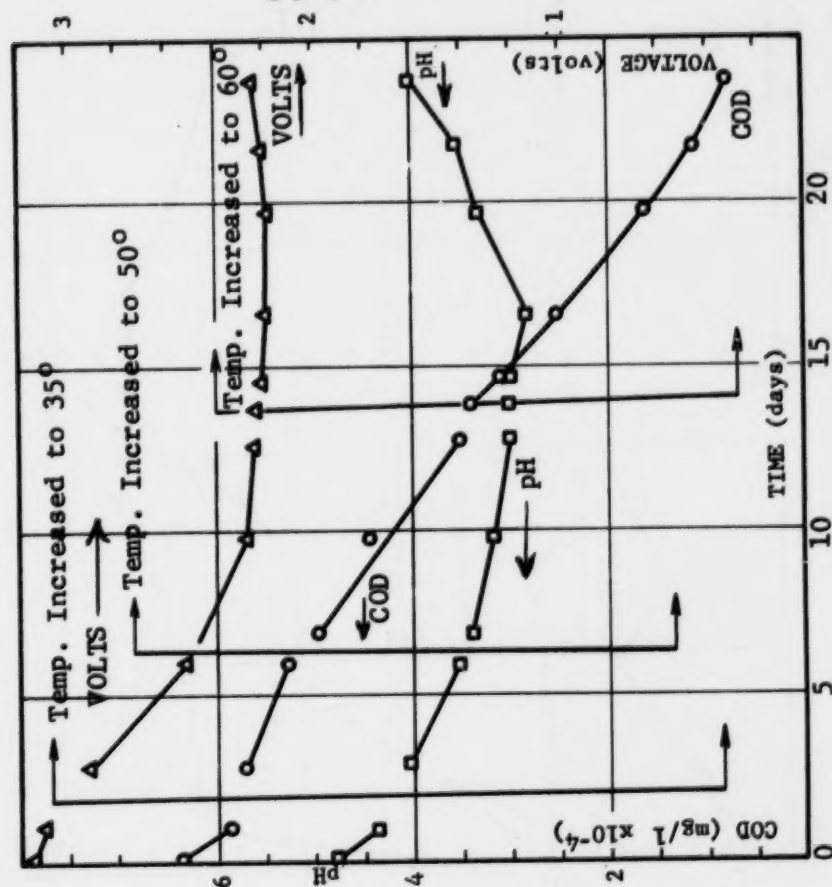


FIGURE 8 RUN: 15
Electrolysis of Acid Whey - Voltage, COD and pH vs Time



CURRENT (AMPS): 3
TEMPERATURE (°C): 35/50/60
AGITATION (ft./sec.): 14.8
STIRRER TYPE: 3 Bladed Propeller

FIGURE 9 RUN: 16
Electrolysis of Acid Whey - Voltage, COD and pH vs Time

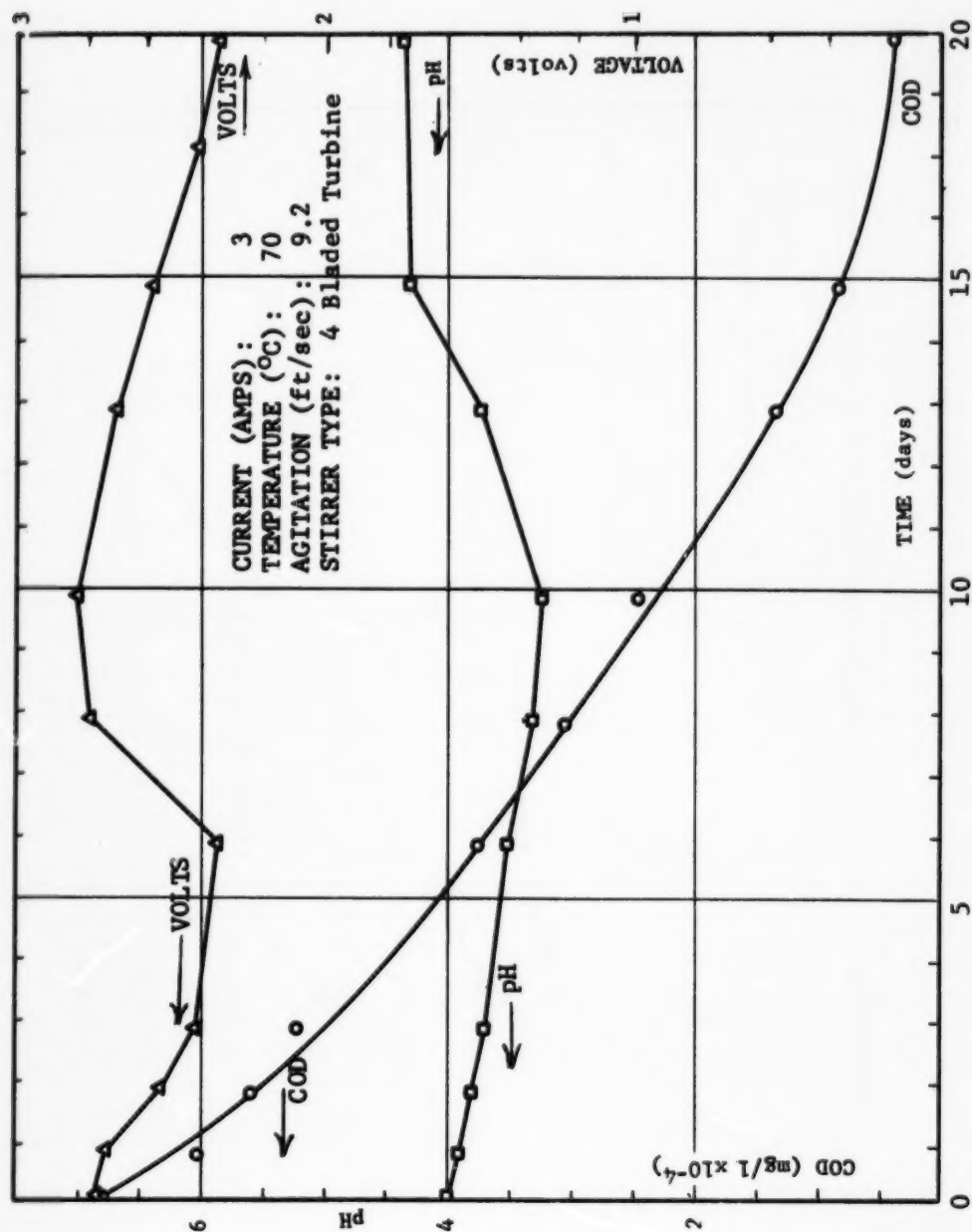


FIGURE 10 RUN: 17
Electrolysis of Acid Whey - Voltage, COD and pH vs Time

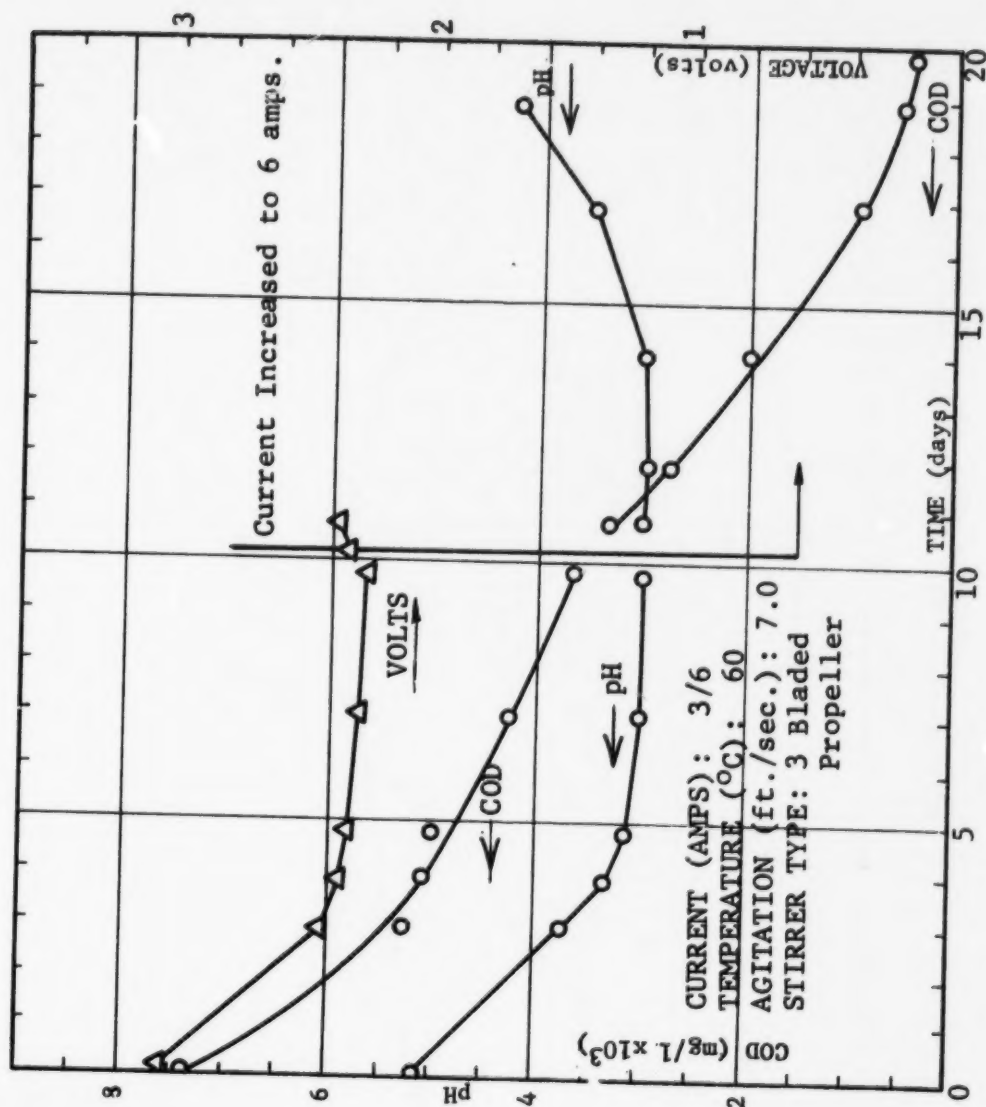


FIGURE 11 RUN: 18
Electrolysis of Acid Whey - Voltage, COD and pH vs Time

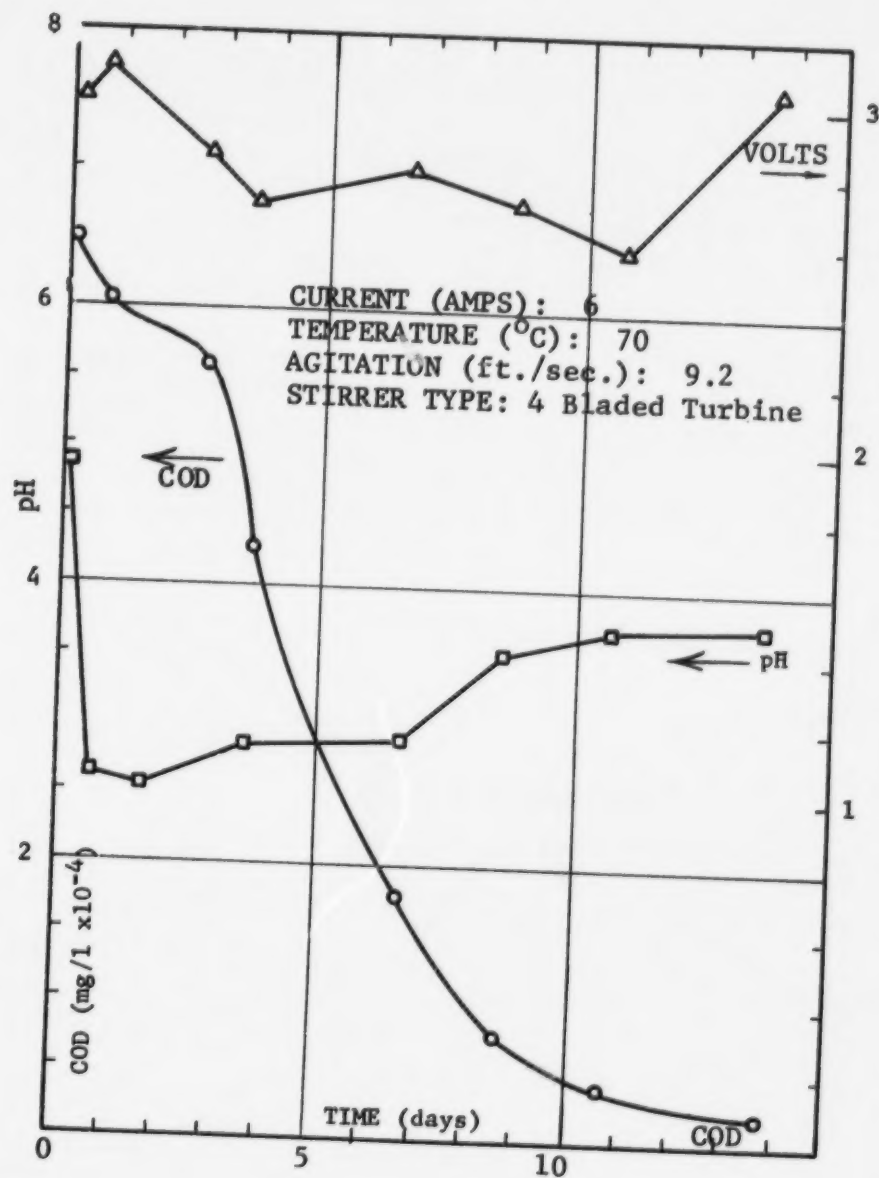


FIGURE 12 RUN: 19
Electrolysis of Acid Whey - Voltage, COD and pH vs Time

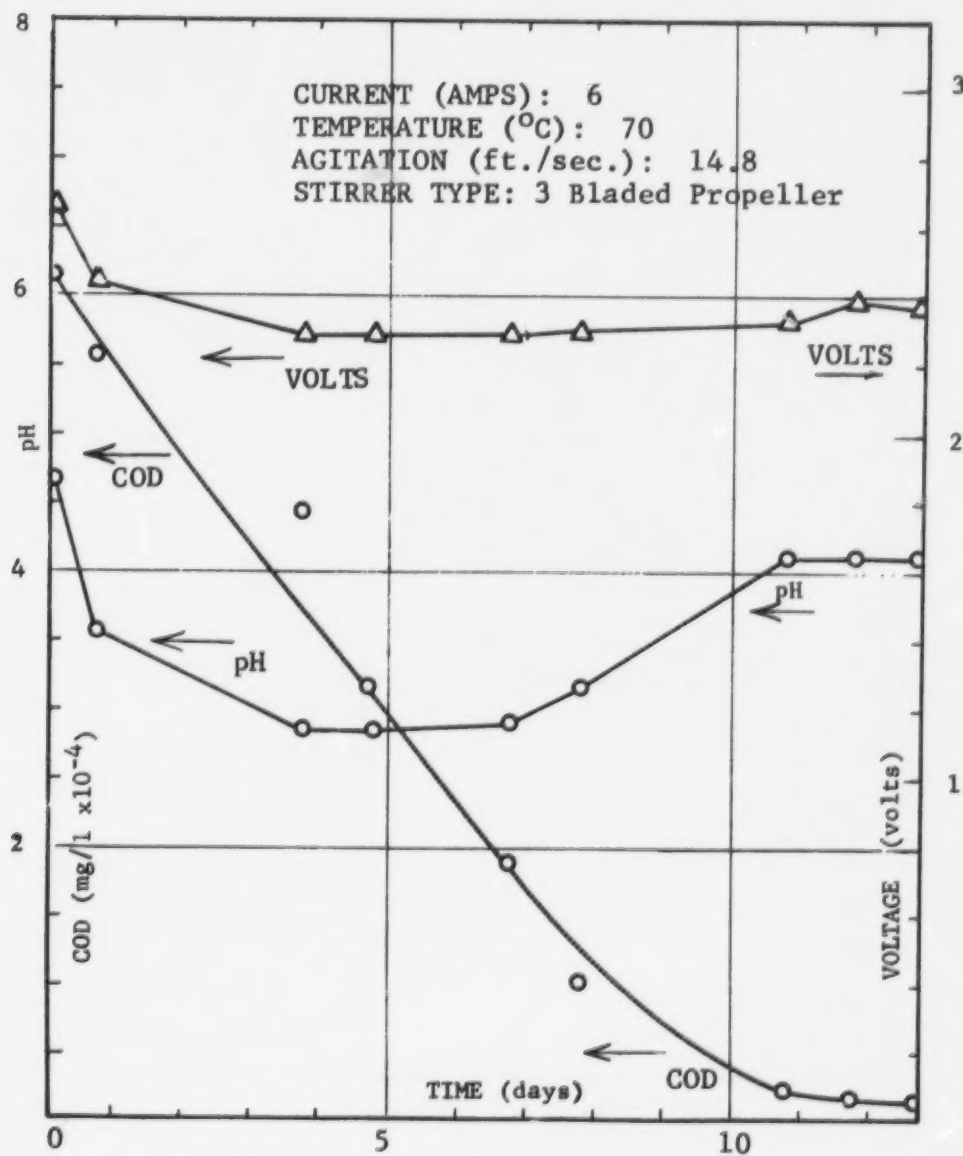


FIGURE 13 RUN: 20
Electrolysis of Acid Whey - Voltage, COD and pH vs Time

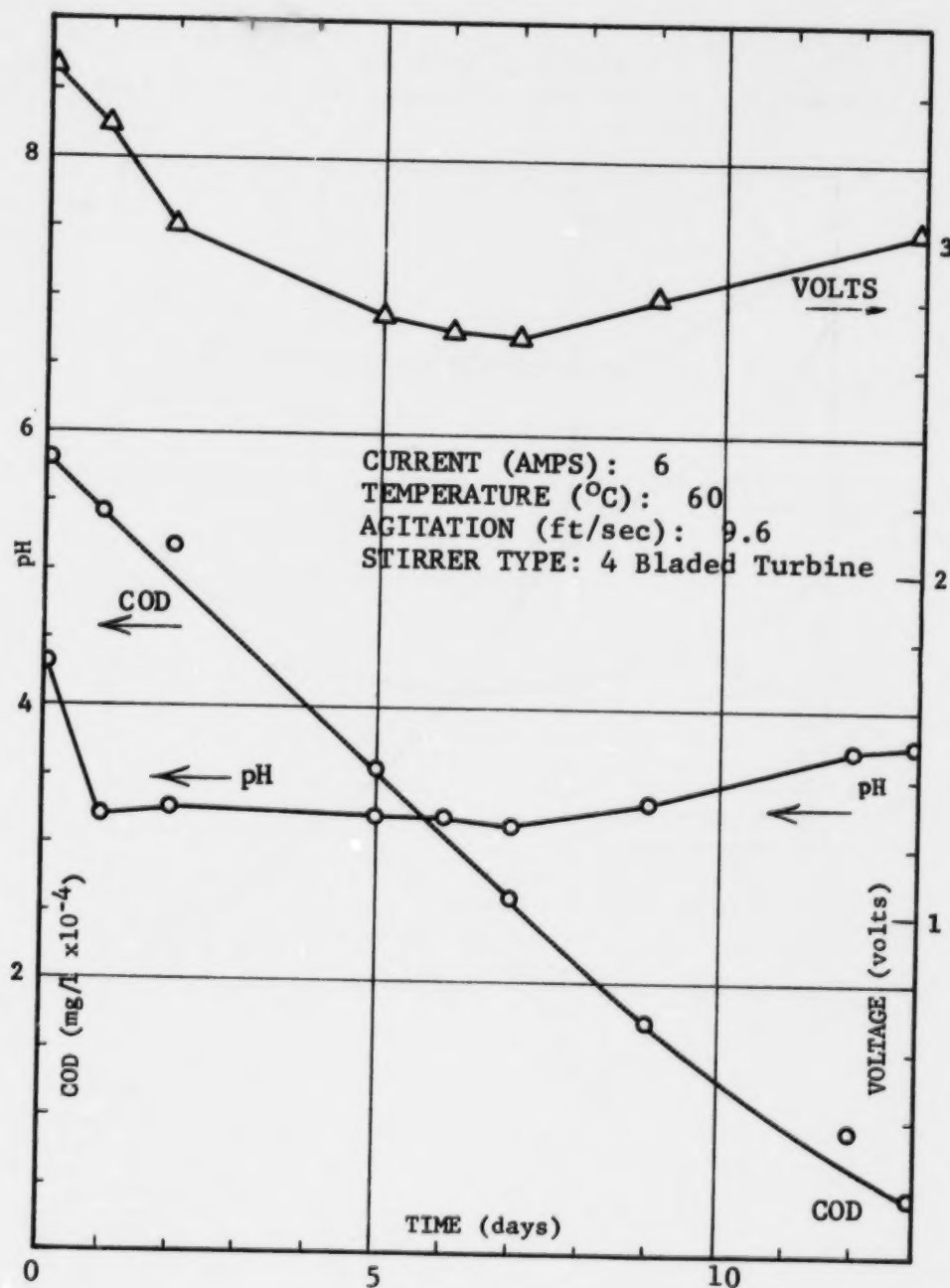


FIGURE 14 RUN: 21
Electrolysis of Acid Whey - Voltage, COD and pH vs Time

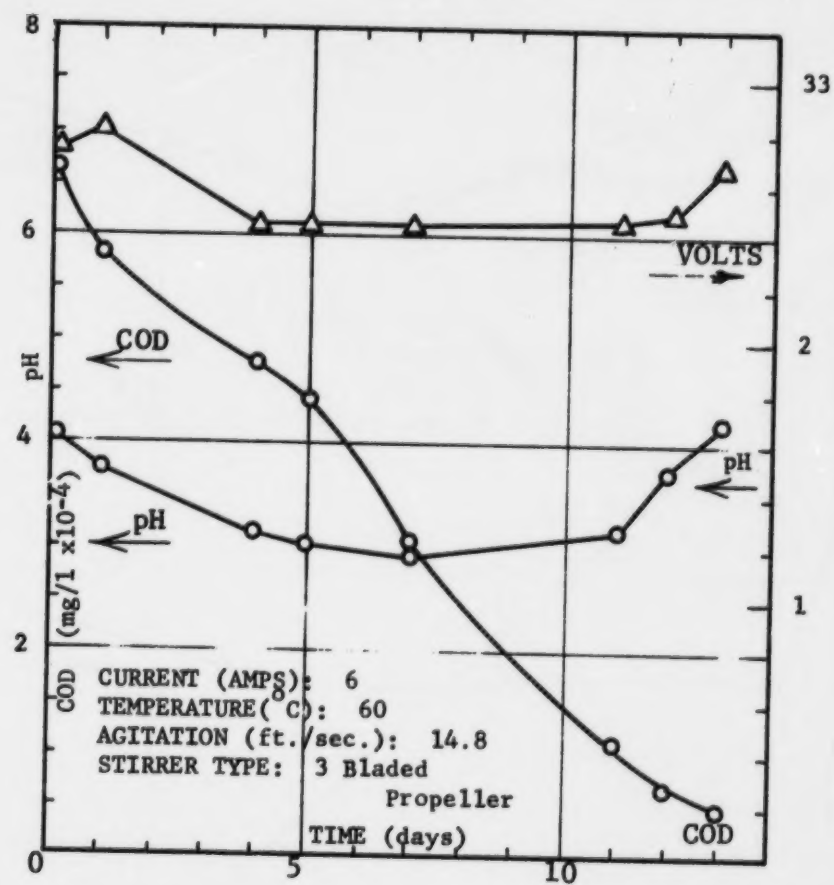


FIGURE 15 RUN: 23
Electrolysis of Acid Whey - Voltage, COD and pH vs Time

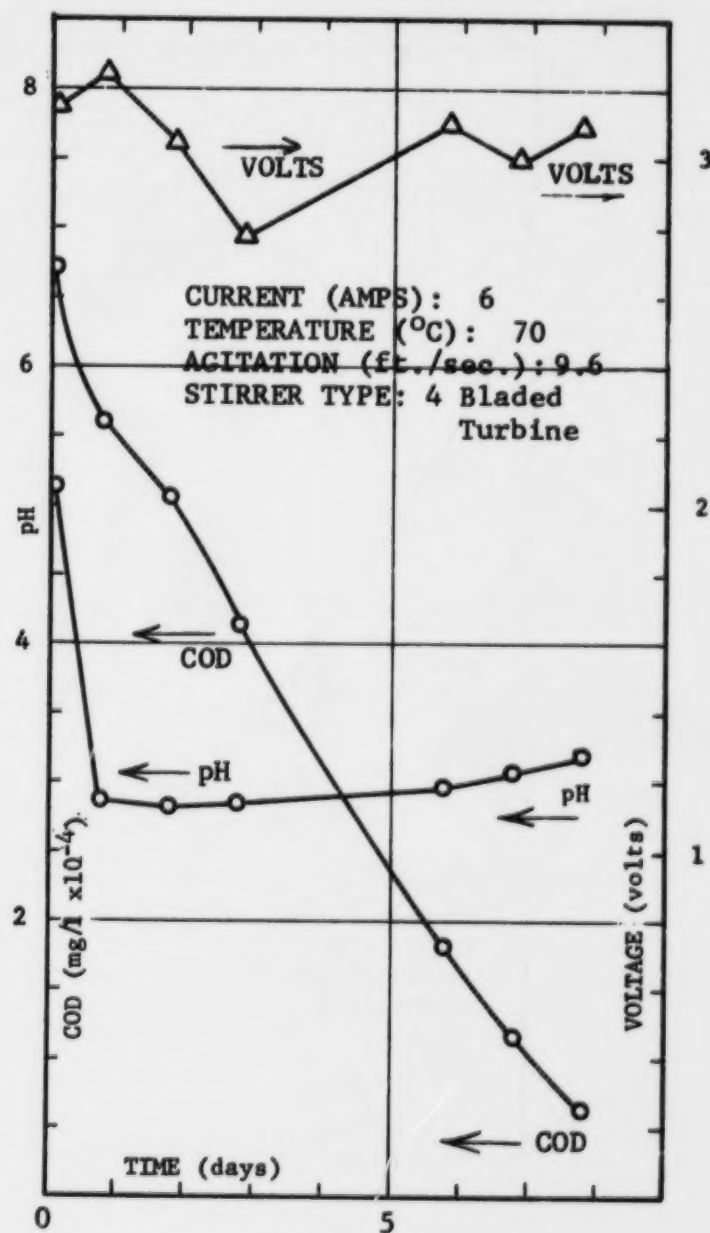


FIGURE 16 RUN: 24
Electrolysis of Acid Whey - Voltage, COD and pH vs Time

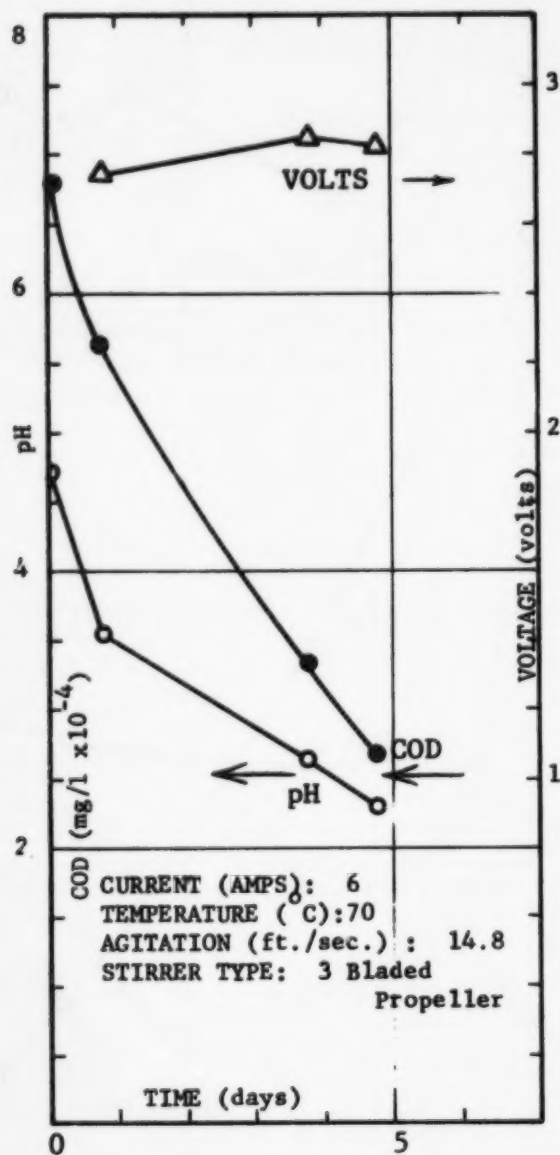


FIGURE 17 RUN: 27
Electrolysis of Acid Whey - Voltage, COD and pH vs Time

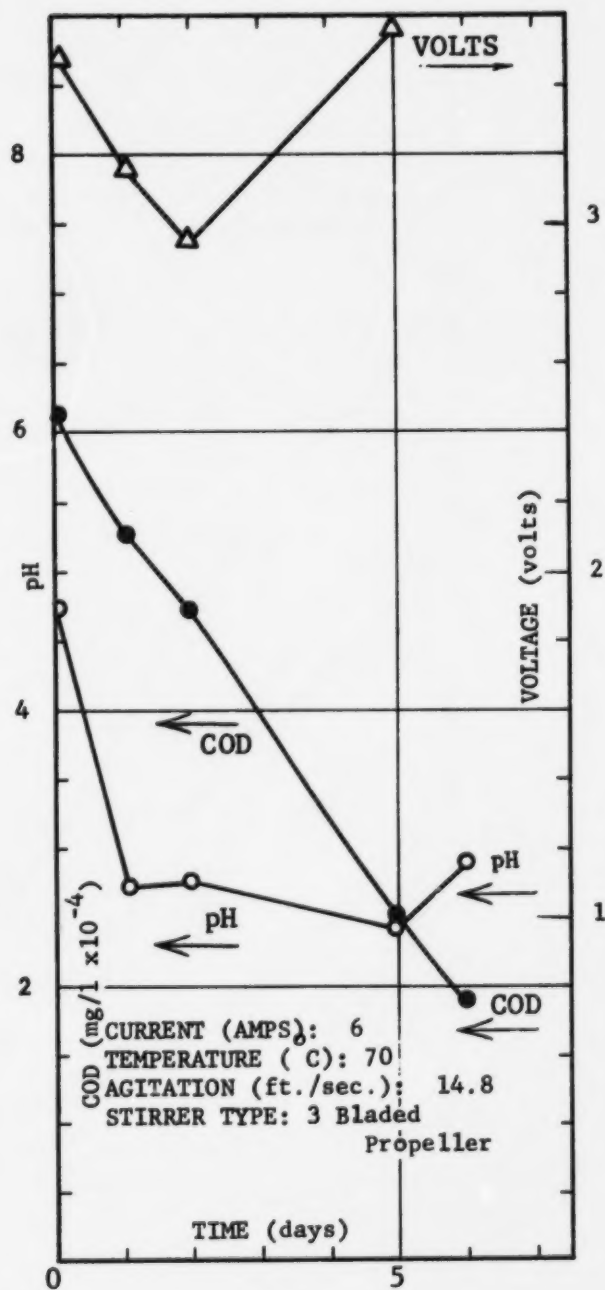


FIGURE 18 RUN: 28
Electrolysis of Acid Whey - Voltage, COD and pH vs Time

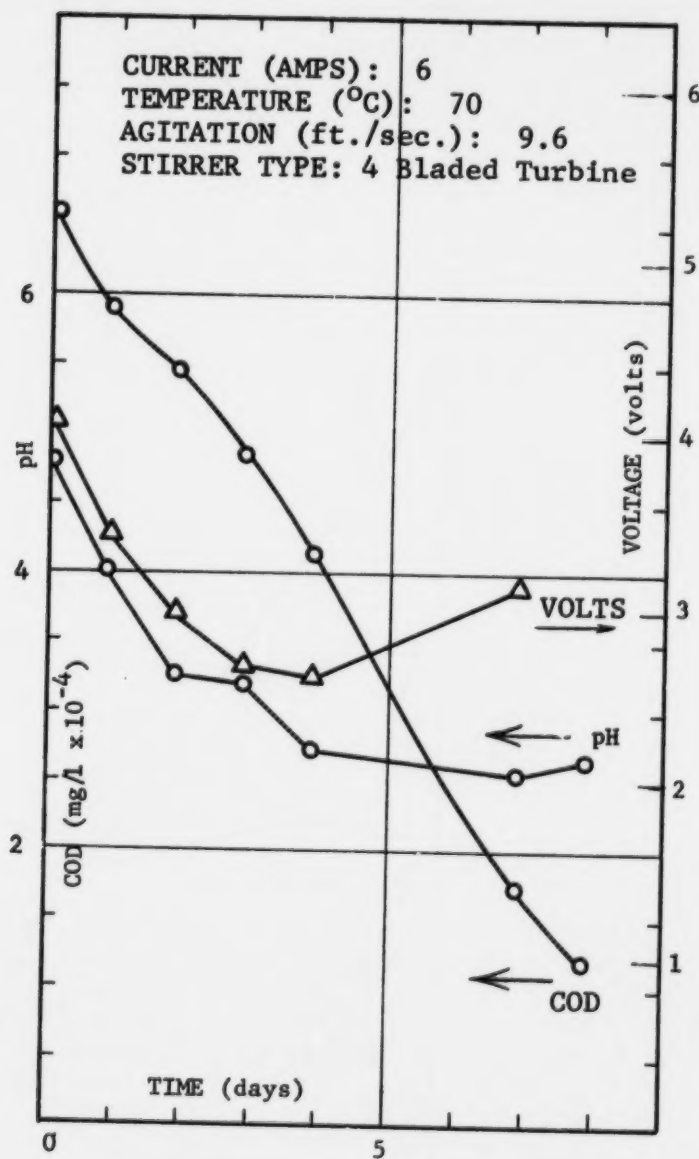


FIGURE 19 WAS MISSING FROM ORIGINAL
MANUSCRIPT

FIGURE 20 RUN: 30
Electrolysis of Acid Whey - Voltage, COD and pH vs Time

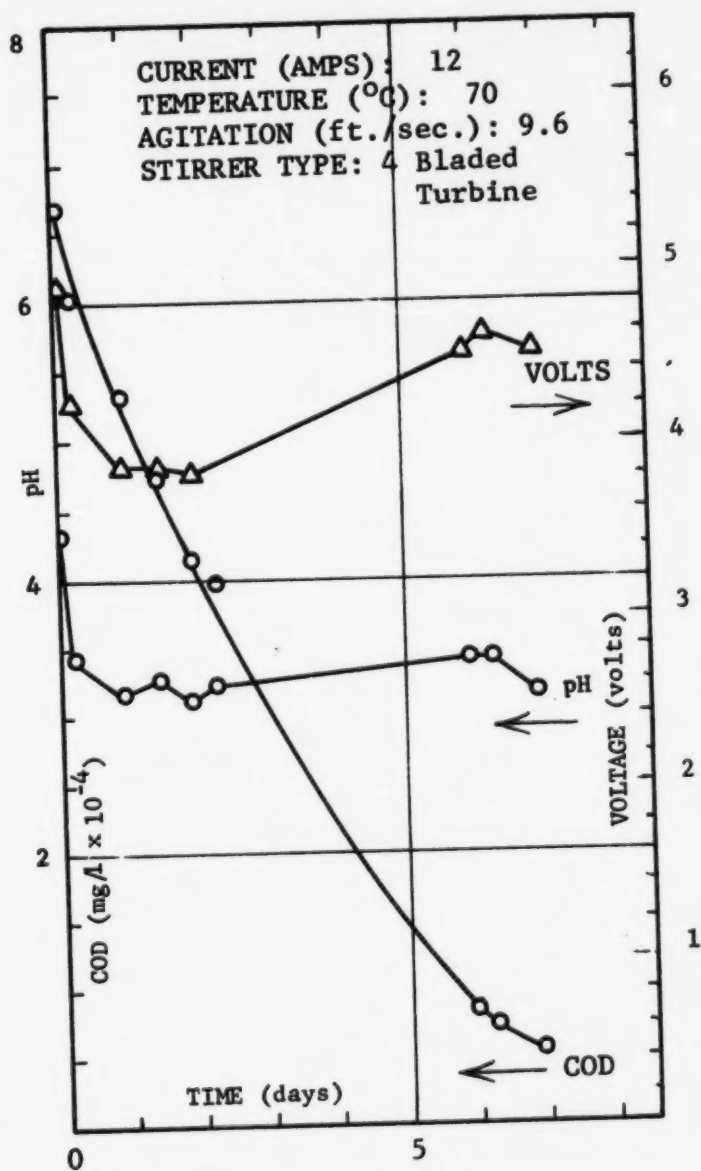


FIGURE 21 RUN: 31
Electrolysis of Acid Whey - Voltage, COD and pH vs Time

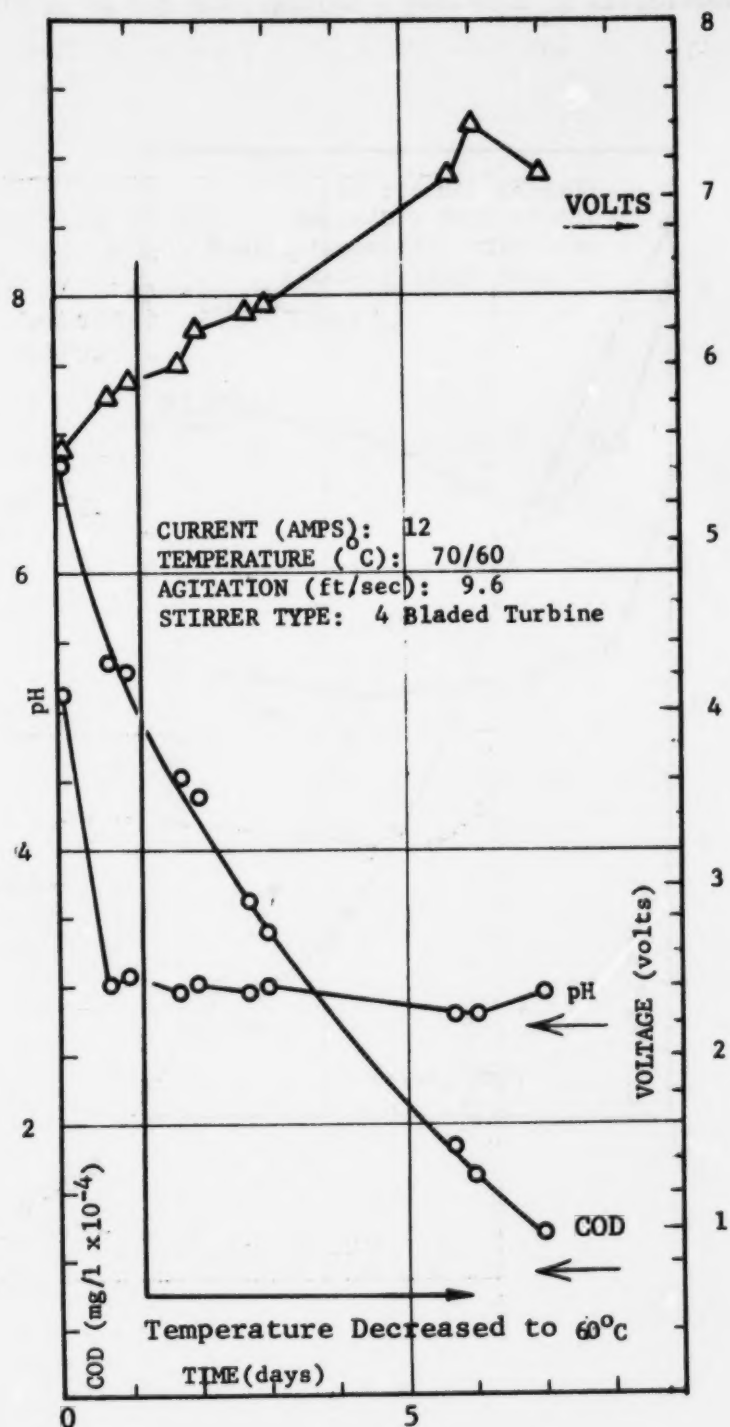


FIGURE 22 RUN: 32
Electrolysis of Acid Whey - Voltage, COD and pH vs Time

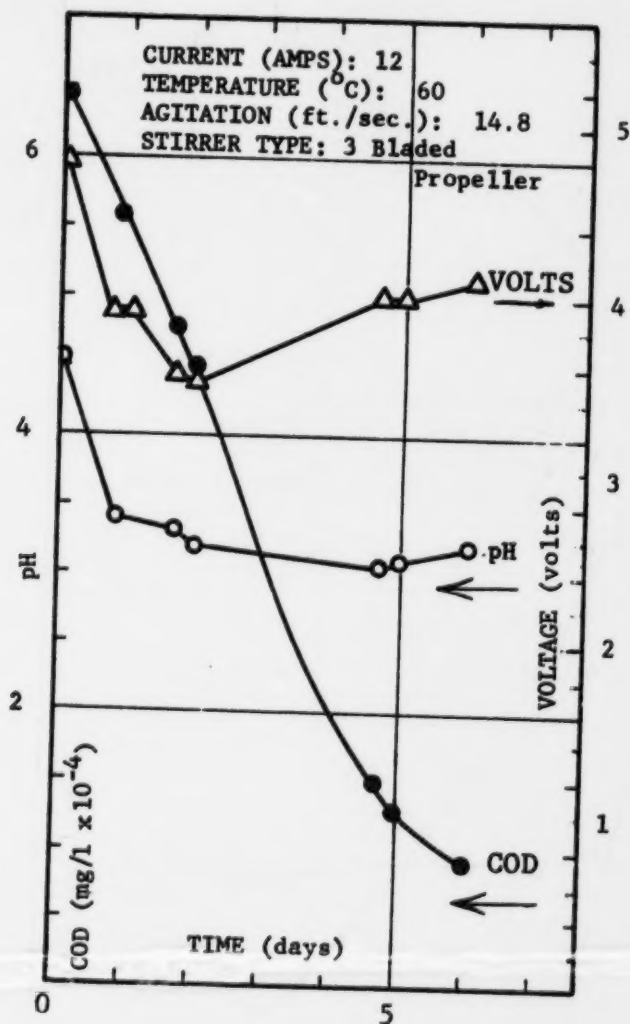


FIGURE 23 RUN: 33
Electrolysis of Acid Whey - Voltage, COD and pH vs Time

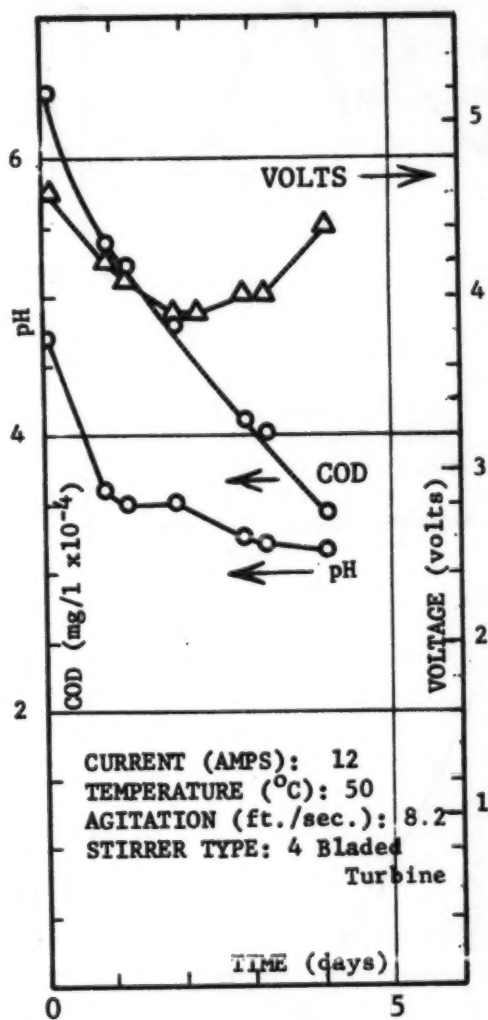


FIGURE 24 RUN: 34
Electrolysis of Acid Whey - Voltage, COD and pH vs Time

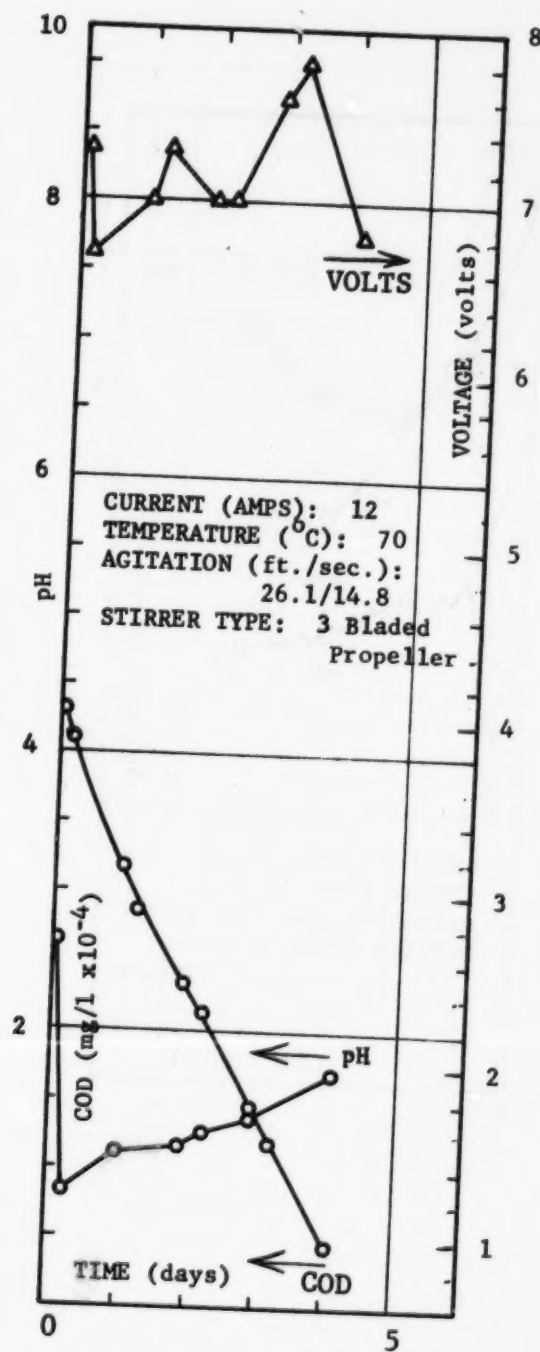


FIGURE 25 RUN: 35
Electrolysis of Acid Whey - Voltage, COD and pH vs Time

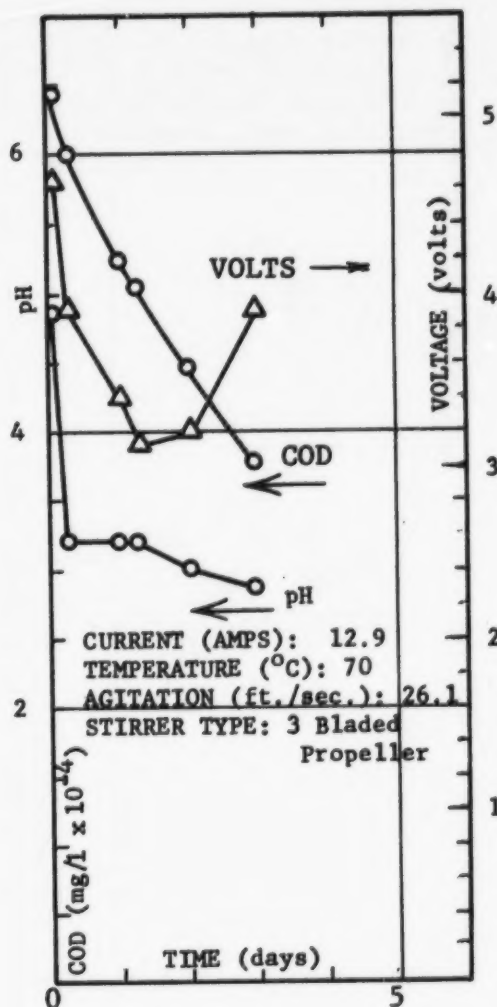


FIGURE 26 RUN: 37
Electrolysis of Acid Whey - Voltage, COD and pH vs Time

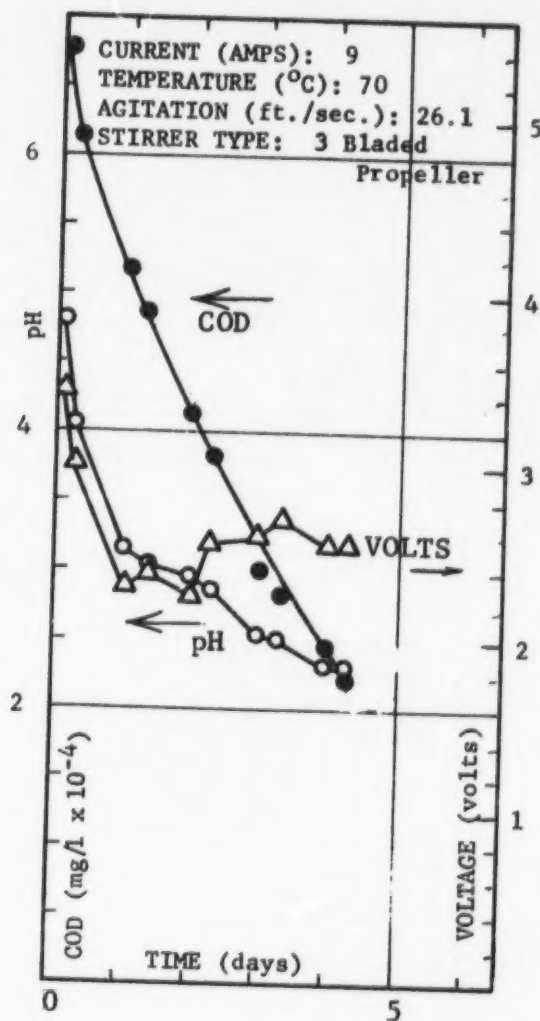
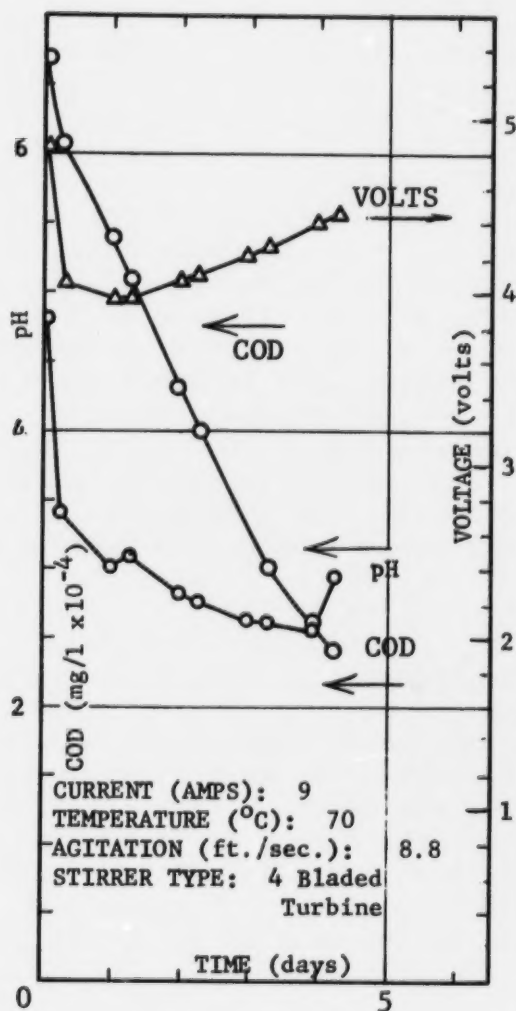


FIGURE 27 RUN: 38
Electrolysis of Acid Whey - Voltage, COD and pH vs Time



The reason for the complex effect of agitation intensity on the current efficiency is probably related to the increase of mass transfer at the cathode, as well as at the anode, when the intensity is increased. One effect may be beneficial while the other is deleterious to efficient current utilization. Moreover both effects are related to all of the system parameters.

Even for the cell voltage, which would be expected to be reduced by increased agitation intensity, the situation observed experimentally is quite complex and the relationship to agitation intensity is not wholly unambiguous. This cell voltage is a sum of the voltages at each electrode, that which is because of concentration polarization effects in the barrier layers near the electrodes and the voltage which is because of the resistivity in the intervening solution. It is not possible to estimate the relative contribution of each individual component of the cell voltage from the experimental results of this study. Ohmic resistance of the current path within the electrolyte is small relative to the electrical impedance at the electrodes. Observe, for example, that in Run 17 summarized in Figure 10, an increase from 3 to 6 amperes of cell current results in an increase of only 0.15 volt in the cell voltage. This indicates that the major impedance of the circuit is non-ohmic, and therefore not within the solution.

The effect of agitation intensity on cell voltage is most evident at higher current density. Comparing Figures 26 and 27 representing the results of Runs 37 and 38, it is seen that with other conditions being comparable, the cell voltage at 8.8 fps agitation speed is very significantly higher than 26.1 fps. These results are obtained with a cell current of 9 amperes. In these runs which were at 12 amperes the cell voltages are relatively high and difficult to reproduce. There was also some evidence of cathode scale formation and anode corrosion in some of the runs at this, the highest cell current in these experiments.

Temperature is an extremely important parameter, as is evident from the summary of data in Table 2 and from the

graphs of individual runs in Figures 3-27, there is, under comparable conditions throughout the range of conditions studied, an increase of current efficiency and a reduction of power required as the temperature is increased. The highest temperature in these studies was 70°C. At higher temperatures the evaporation of solution with the gases which are produced in electrolysis becomes extremely high. It is reasonable to anticipate that results at temperatures above 70°C would be still more favorable. This requires a cell system designed to operate under pressure so that the vaporization of water is held within reasonable limits.

The most favorable conditions, based on the energy requirements, were at 9.5 asf (equivalent to 6 amperes of cell current) at a temperature of 70°C and with agitation equivalent to 9.6 feet per second (fps). The mean ampere efficiency under these conditions is 54.9 per cent to reduce the COD by 90 per cent. The DC power requirement is 7.76 kwh per pound of COD removed, or 0.48 kwh per pound of whey, at full strength.

Reference has been made above to three stages of electrochemical oxidation based on pH changes and also based on the rates of COD reduction. Inasmuch as the pH changes are a result of acids formed during the earlier stage and later consumed, it is of interest to relate these changes of COD with pH. This is done in Figures 28-30 for the data obtained in this investigation for the various runs.

Recovery of Protein from Whey

The method of electrochemical oxidation developed in this investigation appears to offer a means for recovery of a considerable part of the protein content of the whey. This protein, which is rich in albumins and globulins, would be of considerable value to the food industry for baked goods or

FIGURE 28
Electrolysis of Acid Whey - Solution pH vs COD at 3 Amps

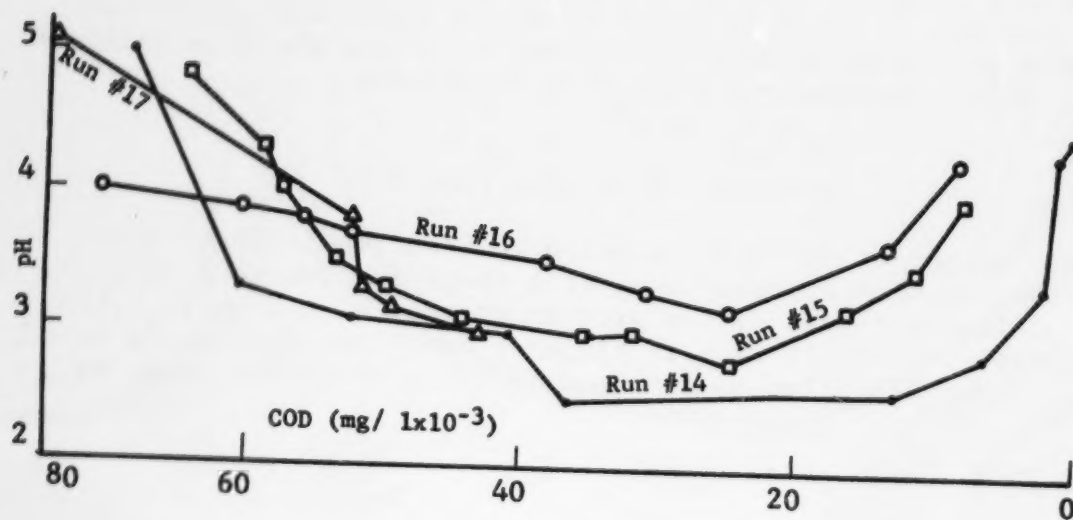
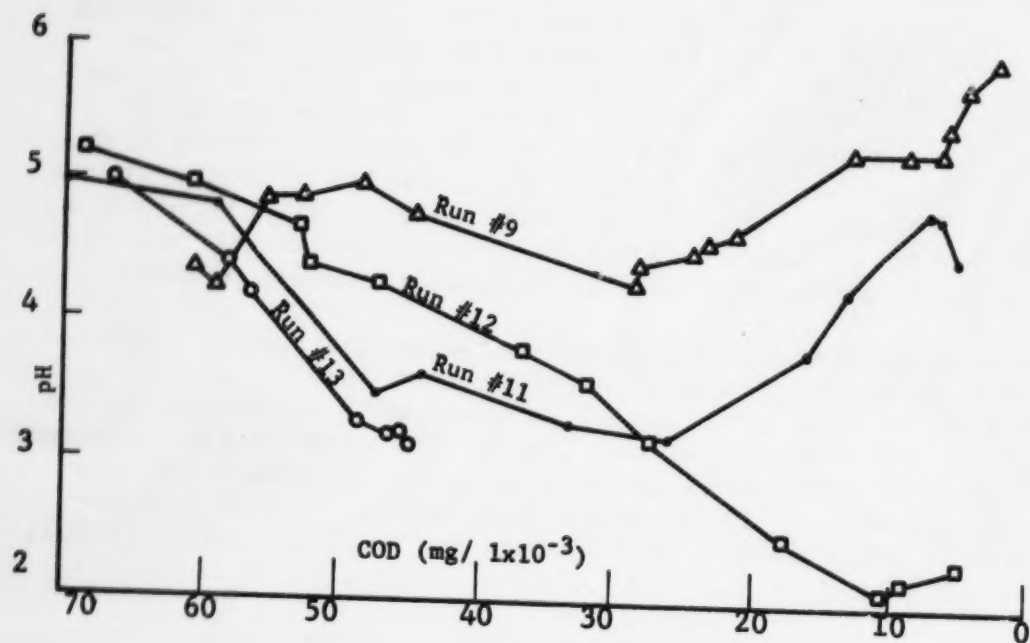


FIGURE 29
Electrolysis of Acid Whey - Solution pH vs COD at 6 Amps

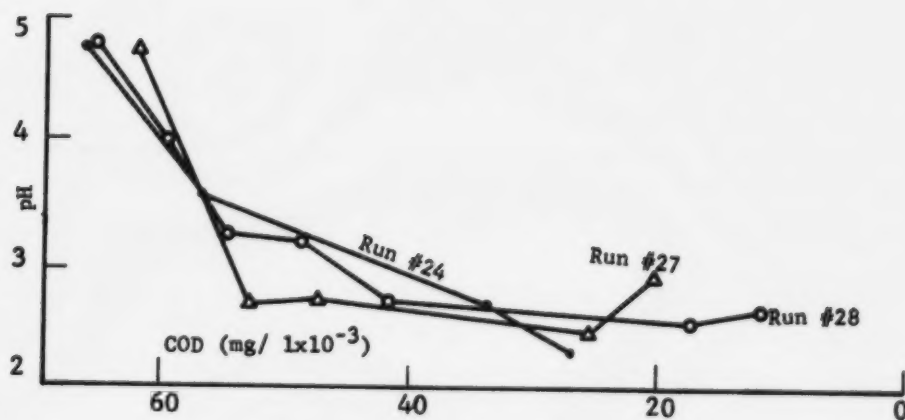
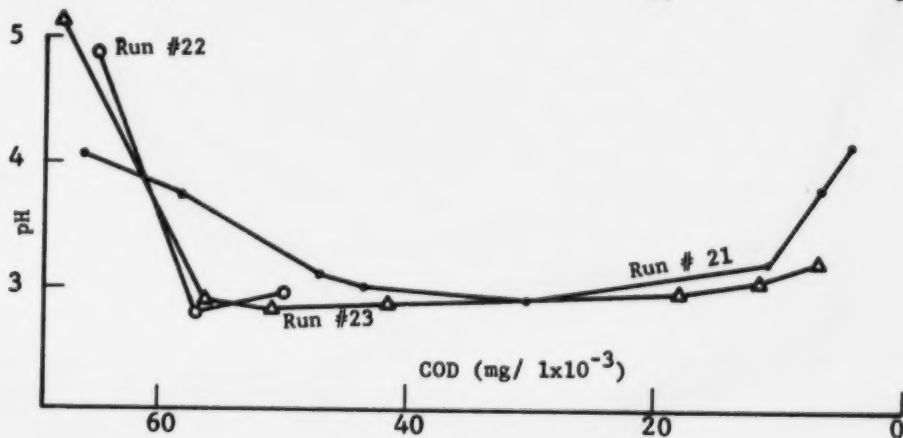
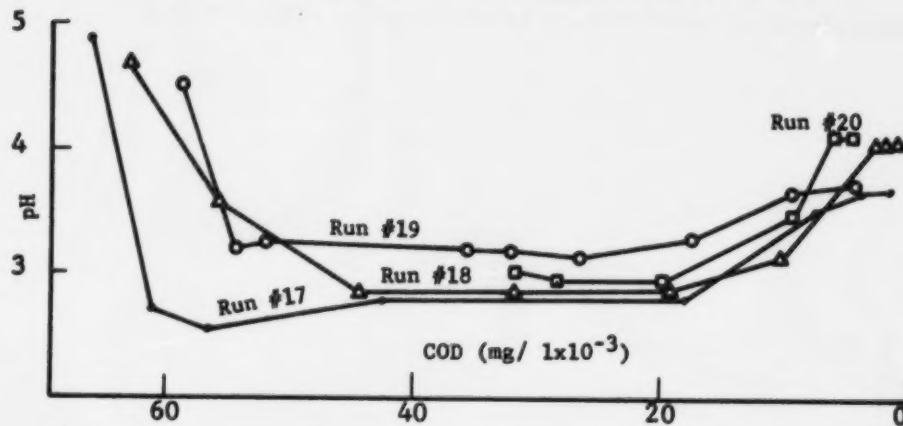


FIGURE 30
Electrolysis of Acid Whey - Solution pH vs COD at 9 Amps

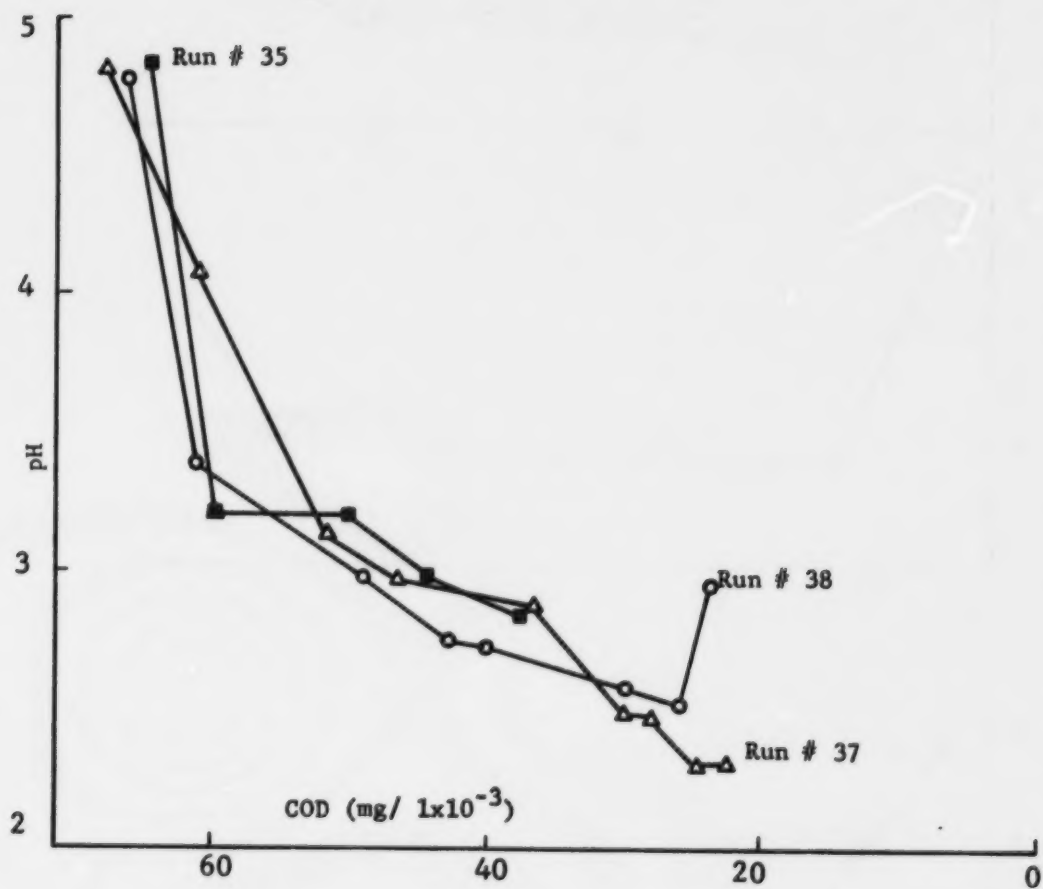


FIGURE 31
Electrolysis of Acid Whey - Solution pH vs COD at 12 Amps

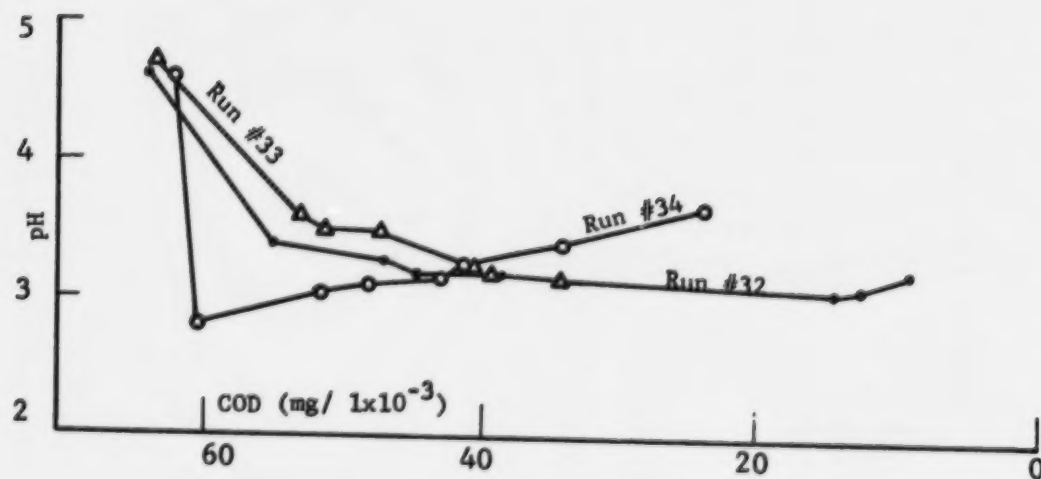
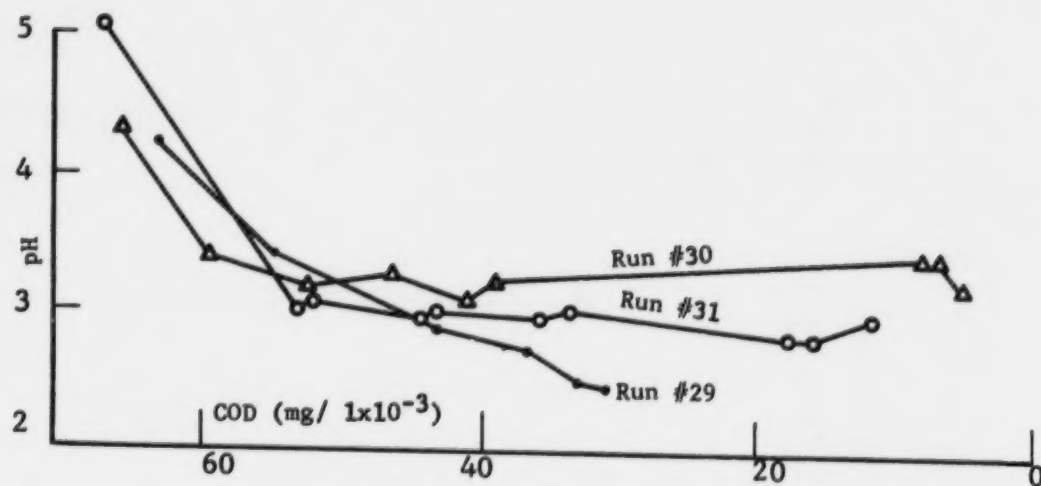


TABLE 2

Current Efficiency and Power Requirements at 3, 6, 9 and 12 Amps

Agitation (ft/sec)	Current (amp)	Blade Type	Current Efficiency (%)				Power Requirement (kw-hr/lb oxygen)			
			35°C	50°C	60°C	70°C	35°C	50°C	60°C	70°C
8.0	3	2 propeller	19	39			20	9		
7.0	3	3 "	19		35		25		10	
14.8	3	3 "	19	35	43		21	10	8	
17.5	3	3 "	29				14			
9.2	3	4 turbine	33	43	47*	59	14	10	9*	7
7.0	6	3 propeller			29				13	
14.8	6	3 "			35	45			11	8
						52*				8*
9.2	6	4 turbine				50				10
9.6	6	4 "				55				8
				32		53		14		9
26.1	9	3 propeller				50				10
						35				15
8.8	9	4 turbine				51				8
14.8	12	3 propeller				47				14
				37		50		17		12*
26.1	12	3 "				29				43
8.2	12	4 turbine		22		31				40
9.6	12	4 "						29		
					32	35*			31	18*

* Volume control unsatisfactory

as an additive to the casein of cheese. In contrast, the lactose, though a major component of whey and though useful as an infant food supplement and for tableting, would never find markets for more than a fraction of that which could be produced.

In addition to investigating the areas relating to oxidation of whey as originally proposed, we have also determined the feasibility of collecting the whey protein as a concentrate in the froth generated during the electrolysis. This was done in Runs No. 5 and 6 in which the whey was oxidized at ambient temperature. Here the froth was collected during the run and analyzed. The remaining whey solution was also collected and analyzed.

These results summarized in Table 3, are indicative of the possibility of recovering a substantial portion of the protein from the whey by collecting the froth. Thus, in Run 6 almost 60 per cent of the whey protein is recovered in the froth which, on drying, produces a solid containing 25 per cent protein and a minor amount of ash.

It is clear from a study of the composite content of protein in the samples from Runs 5 and 6 that the former contained 17.53 grams of protein, or 0.75 per cent whereas the latter contained 26.62 grams, or 1.25 per cent of the whey. The difference reflects a variation in the conditions of curdling in these experiments which is reflected in the protein distribution between the curd and the whey. Not unexpectedly the froth recovery of the protein was higher from the higher protein-containing sample.

Carbon Adsorption

Activated carbons have been used to remove color bodies from sugar solutions since they do not have a marked adsorption affinity for either sucrose (a disaccharide) or for the invert sugars (monosaccharides). Adsorption of lactose (disaccharide) is also comparably weak.

Although activated carbon has been proposed and is used in

TABLE 3
Froth Separation of Whey

	Run No.	Composition				Percent Distribution			
		Volume (ml)	Solids (gm)	Protein (gm)	Ash (gm)	Volume (ml)	Solids (gm)	Protein (gm)	Ash (gm)
Remainder	5	1,900	160.5	9.33	20.32	70.85	77.8	53.2	87.14
Froth	"	450	45.8	8.20	3.00	19.15	22.2	46.8	12.86
Composite	"	2,350			23.32	100.00	100.0	100.0	100.00
Remainder	6	1,700	115.4	10.78		80.2	64.75	40.4	
Froth	"	420	62.8	15.84		19.8	35.25	59.6	
Composite	"	2,120				-	-	-	-

tertiary treatment of waste waters, the treatment is relatively ineffective for the removal of COD generated from carbohydrates. Cheese whey waste, therefore, responds to treatment with activated carbon only to the extent that the nitrogenous substances are removed, and the lactose tends to pass on through the carbon adsorbent.

It appears, however, from the limited data of this investigation, that the electrolytic oxidation products of lactose are readily and strongly absorbed by carbon as shown in Table 4. These oxidation products consist largely of carboxylic acids which are easily produced by the electrolytic oxidation of whey. If carbon is added to the oxidized whey solution and allowed to equilibrate, the COD loading absorbed by the carbon is related to the concentration in mg/l of COD in the filtered solution. This relation can be expressed, at least over a portion of the concentration range, by a Freundlich-type isotherm which is given by

$$A = BC^{1/k}$$

where A is the adsorption in grams COD/gm carbon, B and k are constants and C is the solution's concentration in mb/l of COD.

As stated above, in Run 6 nearly 60 per cent of the protein was recovered in a froth. The whey remaining after froth separation of this protein was 80.2 per cent of the original volume of whey. This solution was then treated with powdered activated carbon in a series of test determinations to establish the adsorption isotherm of the carbon with respect to COD. The carbon, Darco G-60, was selected as representative of an adsorbent which has been tested and used in waste water treatment.³⁰

This study included only 5 test determinations on a single treated whey solution. It is possible therefore only to draw some very tentative conclusions from the results which are summarized in Table 4. The carbon loading is estimated for each test from the difference in COD of the solution before and after treatment with the carbon. In the test which is

summarized in the last row of the Table the quantity absorbed is only 2.57 mg of COD out of 70 mg in the solution. This adsorption is subject to considerable uncertainty because it is derived from the small difference between two relatively large quantities, each of which is subject to analytical error. Thus a small percentage error in each of the two analyses may result in a relatively large error in the carbon loading. It is for this reason that the data summarized in the last column of Table 4 is not considered very reliable.

TABLE 4

Adsorption of COD by Activated Carbon

<u>Carbon Added</u> <u>gm/100 ml</u>	<u>COD in Filtrate</u> <u>mg/l</u>	<u>COD Adsorbed</u> <u>mg</u>	<u>COD Loading</u> <u>mg/gm Carbon</u>
25	31	66.9	2.7
5	27	67.3	13.4
0.5	360	340	68
.05	640	60	120
.005	670	30	600

Each determination was performed by dilution of 1 ml of the oxidized whey with water to 100 ml and subsequent addition of the quantity of carbon indicated in the first column of Table 4. A determination of the COD concentration before and after treatment was then made. The difference represents the change which is the result of adsorption. When this quantity is converted to milligrams per gram of carbon added to the solution, it represents the loading of the adsorbent.

From a log-log plot of the experimental data, the best linear representation corresponds to the Freundlich isotherm

$$A = 0.132 C^{1.13} \pm 20\%$$

where A is the mg/gm adsorption of COD and C is the solution concentration, mg/l.

In a commercial process, the spent carbon, loaded with the oxidation products from the electrolytic oxidation of whey would be regenerated by thermal treatment. This has been accomplished in other projects for advanced waste treatment. From the loading of the carbon which has been found, there is the possibility of approaching 1,000 mg of COD adsorption per gram of carbon. This is many times the loading in conventional waste treatment with adsorbent carbon.

There is a possibility that, in view of this high loading, the calcined carbon will exceed in quantity the amount which is used for treatment. If this is in fact the case, there is a net output of carbon. The extra carbon is derived from the calcination of the carbohydrate-derived adsorbate.

It needs to be determined whether the regenerated carbon may be processed to develop adsorption characteristics which are comparable with those of the carbon used in these tests. As a matter of fact, it is necessary to demonstrate that these characteristics are maintained even after many cycles of treatment and regeneration. The present study is not intended to establish the commercial feasibility but merely to explore the potential for development.

Electrolytic Oxidation

At a current efficiency of 100 percent and with a cell voltage equal to the decomposition potential of water, the electrical energy to remove a pound of COD is 1.867 kwh. The best result obtained, based on energy requirement, is 6.68 kwh. This was obtained using the following conditions: 70°C, 9.2 ft/sec agitation rate and a low current density (3 amps or 4.75 asf) as shown in Table 2. It is probable that still higher temperatures, requiring pressurized cell construction, would yield still better energy efficiency.

Substantially, the same efficiency is obtained at higher current density using higher stirrer speeds. This is indicative of the importance of mass transfer at the electrode surfaces in enhancing electrochemical oxidation. At comparable agitation and current density, the efficiency is improved as the

temperature is increased. The maximum operating temperature was 70°C which, in an open vessel, was the practical upper level in order to avoid excessive vaporization. Improvements may be expected if a closed system is used.

During the electrolytic oxidation, as the COD is reduced, there is a point at which further reduction is more difficult and less efficient. Under suitable conditions, a reduction of at least 90 percent is possible while, with some sacrifice of efficiency, virtually complete removal of COD is feasible. To reduce one pound of COD per day requires 8.68 square feet of electrode area, assuming 14.25 amp/sq ft and 51.2 percent current efficiency.

By way of comparison a plant treating one million gallons per day (MGD) of waste containing about 1,000 mg/l of COD was estimated to cost \$650,000, or about \$78 per daily pound of COD. To be competitive, a plant based on electrochemical oxidation (of whey) would have to cost no more than \$78 for 8.68 square feet of electrode area, or about \$9 per square foot including all accessory equipment and other costs. This is not outside the design capability. The cost comparison with conventional treatment becomes much more favorable with smaller plants, typically those producing whey in which the unit capital investment for conventional biological treatment is much higher than the \$78 per daily pound of COD.

The cost allowance per square foot of anode surface in the methods of this study must include provision for rectifiers and process equipment such as tanks, pumps, piping and instrumentation. All of these costs vary with the design capacity, which requires engineering studies beyond the scope of the present study.

A most important economic consideration is that of power cost for approximately 7.5 kwh per pound of oxygen demand. This is considerably more than for biological oxidation but there are benefits in process simplicity, equipment size and material handling which may compensate for this increased power requirement. This will depend on power rates and on the design capacity.

The electrochemical system which was developed in this study transforms the organic waste, ultimately, to carbon dioxide, water and nitrogen. There is no attendant problem of clarification, sludge handling or sludge disposal. Whey flows into the system and water containing dissolved salts flows out. Supervisory costs other than for power should be nominal.

With design of a compact electrode assembly, the system should be small in size and the effluents clear and sterile having only a mild vinegar odor which disappears on dilution, or on continuing the electrochemical oxidation (at reduced efficiency) to near completion.

SECTION VII

DISCUSSION

During the course of this investigation two methods for decreasing the COD level became evident. These are, based on two bench scale runs and a limited number of adsorption test determinations,

1. separation of whey proteins in the froth prior to electrochemical oxidation decreases the COD of the resulting whey, giving a solution containing 60 percent of the total whey protein as a 25 percent concentrate, and/or
2. removal of the oxidation products from the whey electrolysis by carbon adsorption. This is feasible since the intermediate oxidation products of the whey are carboxylic acids which are readily absorbed by the carbon.

These methods could be used in conjunction with the electrolytic oxidation to decrease the COD of whey and are discussed below.

Froth Separation

The procedure to form a froth and, subsequently, to collect the froth has certain advantages when used in conjunction with the electrolytic oxidation of whey. Of significance, froth separation in a small or moderate capacity plant is much more attractive economically than is evaporation and drying. Furthermore, the economic value of whey is principally in the protein. Froth separation enhances this value by separating the protein from both the lactose and the salts which are in the whey.

With limited experimentation of this process it has been found that 60 percent of the total protein of the whey could be recovered in the froth. The protein was present as a

25 percent concentrate. Optimization of this process would

1. decrease the electrical requirement for oxidation of the whey, and
2. yield a concentrate amenable to subsequent electrodialysis or ultrafiltration for purification and concentration of the protein values.

The recovery of a considerable portion of the protein of the whey by froth separation prior to further treatment to eliminate lactose is also potentially very attractive since it would lower electrochemical energy requirements.

Adsorption of Oxidation Products by Carbon

The use of activated carbon in conjunction with partial electrochemical oxidation of the lactose of whey results in a high loading of the carbon. This presents an alternative method of COD removal which requires a much smaller electrode installation. The method of carbon adsorption is applicable to treatment of daily plant washings as well as to the more concentrated whey. The problems of regeneration of the carbon are yet to be explored.

Activated carbon has found application in the tertiary treatment of waste water, that is, on a feed consisting of clarified effluent of biological treatment. In a comparison of prior applications of activated carbon with that of the present study, the following generalizations are to be considered:

1. In well treated, clarified secondary effluent,²³ very little organic material escapes from a column containing unspent carbon.
2. If the secondary treatment is poor, as with raw whey, there usually is breakthrough of soluble organics even when the carbon is new. This result should be expected since certain groups of materials in poorly treated waste water and in raw whey are known to resist adsorption on carbon. To demonstrate the poor adsorbability of some examples from some

of these groups, batch adsorption tests were conducted by Bishop et al²³ using one gram of powdered carbon per liter of solutions of various pure substances.

3. Electrochemically, partially oxidized whey contains substances which, because of their concentration and tendency to adsorption, permit much higher carbon loadings than are possible in tertiary treatment of waste water.

Inasmuch as the cost of physical loss of carbon in regeneration is the major item of cost in carbon treatment of waste water, the possibility of a self-sustaining carbon regeneration appears to warrant further study. The possible combination of froth recovery of protein combined with activated carbon removal of electrochemically oxidized lactose is an economically attractive possibility.

It is of interest to compare the data (represented in Figure 2), which was obtained in this study, with that of Allen et al²⁴ in which secondary effluent was treated with activated carbon, both virgin and reactivated. Both of these are more highly loaded for equivalent COD in the effluent solution than in the case of electrochemically oxidized whey. The whey, being much more concentrated than any secondary sewage effluent, should permit a higher loading of COD/lb of carbon. This might ultimately reach as high as 50 pounds COD/100 lb of carbon for whey compared to about 35 pounds COD/100 lb for secondary effluent, assuming a system of whey-carbon contacting. This is, however, based on somewhat questionable extrapolation from present data.

In practice, the actual design capacity for a carbon adsorption system with secondary effluent is from 50-100 percent higher than the isotherm capacity. This apparent increase in loading is probably a result of biological activity.²⁴

It is evident, therefore, that additional effort aimed at combining the pre-elimination of COD in whey by froth collection, followed by electrolytic oxidation and the removal of COD by carbon adsorption may yield an economically, attractive

process, particularly if the carbon is regenerated and, if in fact, extra carbon can be derived from the calcination of carbohydrate derived adsorbate.

Alternate Methods

There are a number of alternative methods which are under development to utilize the components of cheese whey. It is possible to recover protein by acidifying the whey and then centrifuging. Another method is ultrafiltration to retain the protein and allow passage of the lactose and salts. Still another method is to demineralize whey by electrodialysis and then concentrate and cool to crystallize the lactose. There are also various possible combinations of these means.

When utilizing ultrafiltration, the pressure required is 60 psi at 49°C to recover a 25 per cent protein concentrate. The cost of a plant to treat 250,000 lbs/day of whey has been estimated at \$610,000 and the annual operating cost, \$196,000.²⁵ This operating cost is about 5¢ per pound of contained oxygen demand and it includes the cost of reverse osmosis treatment for lactose recovery. The limited scope of the present study does not permit a firm estimate of the cost of foam recovery of the protein. We did, however, achieve a 60 per cent recovery of the total protein as a 25 per cent concentrate, and this does not necessarily represent the optimum performance of this system.

The greatest drawback of any membrane system for a product which must be sold to the food industry is that of the difficulty of sterilization. Equipment for foam separation may be designed of polished stainless steel which may be sterilized by steam and cleaned with alkaline compounds. Membrane systems are not usually capable of being designed for comparable sterilization, cleaning and inspection.

Following the recovery of the protein as a concentrate, the economic value of the solution containing lactose is marginal. Although there are markets for lactose as a specialty, it is doubtful whether there is the market potential to absorb

large amounts except at a very low price in competition with beet or cane sugar molasses. In most locations, the problem will, therefore, be one of determination or development of the most economical method of disposal while avoiding pollution.

If the treatment is biological, it must be, in part at least, aerobic as stated above. Even raw whey contains insufficient nitrogen to sustain full elimination of oxygen demand. Combination with domestic sewage is the ideal method if it is possible. It provides both dilution and the provision of nitrogen. When this method is not possible because of location, the alternatives are evaporation, reverse osmosis, electrochemical oxidation or a combination including carbon adsorption. All of these, except evaporation, require extensive development before their advantages and limitations may be fully evaluated.

SECTION VIII

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SECTION IX

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